

Application No.: 09/714,658

Docket No.: 53786US012

Remarks

The following remarks respond to the Advisory Action mailed on August 4, 2003.

In the third paragraph of the Advisory Action, the Examiner repeated his previous statement that Hartman expressly teaches that the skin provides the carrier with a smooth face and that the surfaces of the foam article are parallel to the flat or smooth surfaces of the skin layers and adhesive layers. The Examiner pointed out that attorney's arguments are not factual evidence required to rebut a prima facie case of obviousness and must be supported by an appropriate affidavit or declaration. The Examiner instructed Applicants to see MPEP section 2145.1.

Applicants submit that the Hartman patent (U.S. Patent No. 5,476,712, herein referred to as "US '712") itself is evidence and that an affidavit or declaration is not needed to discuss what the patent document expressly or impliedly states. Further, MPEP section 2145.1 refers to MPEP section 716.01(c) for examples of attorney statements which are not evidence and which must be supported by an appropriate affidavit or declaration. The examples include the following: statements regarding unexpected results, commercial success, solution of a long-felt need, inoperability of the prior art, invention before the date of the reference, and allegations that the author of the prior art derived the disclosed subject matter from the applicant. Discussing attributes of an article described in a patent reference is not included in the examples provided in MPEP section 716.01(c).

Applicants direct the Examiner to column 3, lines 14-19 of US '712. This passage provides that "[t]he skin smooths the adjacent outer core which may be roughened excessively by the expansion of the blowing agent. The smoothing of the core face is by a leveling of the roughness resulting from the blowing process. In this manner, the skin provides the carrier with a smooth face." This is factual evidence. The factual evidence is that the core of the article is rough in the absence of the skin layer. The skin layer levels the roughness to provide a carrier layer that is smooth.

Even as the schematic shows parallel lines, the text specifically states that the core is rough and must be smoothed by the skin layer to provide a smooth carrier layer. The Examiner is instructed in MPEP section 2141.02 to consider the reference as a whole. Thus, when considered as a whole, US '712 does not teach a foam having at

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least one major surface that is smooth without being bonded to an additional layer, as recited in claim 1 of the present invention. Rather, this reference teaches a foam having a rough surface that is smoothed only by attachment to another layer (i.e., the skin layer).

In paragraph 4 of the Advisory Action, the Examiner noted the previous argument by the Applicants that the die used in US '712 is designed such that the pressure drops outside the die. Consequently the microspheres are not expanded until the molten material exits the die. The Examiner stated again that Attorney statements are not evidence and must be supported by an appropriate affidavit or declaration.

Again, Applicants submit that US '712 itself is evidence and that no affidavit is required to discuss aspects of the patent that are expressly or impliedly stated. The Examiner is directed to column 7, lines 10-42, portions of which are directly quoted below.

US '712 provides that "[s]ubstantially all of the expansion of the blowing agent is believed to occur just as the polymer begins to flow out of the opening of the die 24 and the pressure applied to the polymer is reduced. In this manner, the blowing agent effects on the core charge are minimal during the coextrusion processing thereof, since it is only at the exit from the extrusion die, e.g., within several inches of the die opening, that substantial expansion of the blowing agent occurs. If expansion of the blowing agent occurs earlier in the extrusion process, there is a tendency for the microspheres to blow out through the skin layer sometimes resulting in a very rough outer layer surface. Excessive pre-blowing can result in an effective loss of the cellular structure." Thus, the reference discloses that the expansion occurs within a few inches of exiting the die. Further, the patent states that "[t]he coextrudate emerging from the die 24 is contacted with a chill roll (not shown) in a conventional manner. This is believed to end substantially all blowing and expansion, and to fix the matrix and void structure of the core 14." This passage further confirms that the expansion is external to the die rather than inside the die. If the material had expanded in the die, there would be no need to use a chill roll to end expansion.

Thus, US '712 teaches expansion external to the die and increasing the dimensions of the foam after exiting the die. In contrast, the foams of the present invention are expanded internal to the die and exit the die in an already expanded state.

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Regarding paragraph 5 of the Advisory Action, the Examiner stated that the argument that a tackifier would need to be added to the A-B-A triblock thermoplastic elastomer to form a pressure sensitive adhesive is not evidence and must be supported by an appropriate affidavit or declaration.

Applicants' submit a copy of a chapter from the following reference as evidence: D. Satas, *Handbook of Pressure-Sensitive Adhesives*, Chapter 11, pp. 220-275, van Nostrand Reinhold Co., New York (1982). Chapter 11 of this book is directed to block copolymers. The text states, starting on the last sentence on page 224, that thermoplastic rubbers have little inherent tack. Therefore, the rubber must be compounded with tackifying resin and, in some cases, with plasticizer to develop the required tack. This reference serves as factual evidence that A-B-A triblock copolymers are not inherently pressure-sensitive adhesives by themselves.

Applicants also submit a copy of several pages from the following reference: A. V. Pocius, *Adhesion and Adhesives Technology: An Introduction*, Chapter 9, pp. 216-217, 230-233, and 244-245, Hanser Publishers, New York (1997). On page 216, the definition of a pressure-sensitive adhesive is provided from the Pressure-Sensitive Adhesive Tape Council. Pressure-sensitive adhesives are defined as materials with the following properties: (1) aggressive and permanent tack; (2) adheres with no more than finger pressure; (3) requires no activation by an energy source; (4) has sufficient ability to hold onto the adherend; and (5) has enough cohesive strength to be able to be removed cleanly from the adherend. The A-B-A triblock copolymers by themselves cannot meet the above definition of a pressure-sensitive adhesive. They do not have aggressive and permanent tack, do not adhere with no more than finger pressure, and do not have sufficient ability to hold onto the adherend when used without a tackifier.

The same reference provides an alternative definition of a pressure-sensitive adhesive using what is known as the Dahlquist criteria (see Pocius, pp. 230-233). In summary, if the modulus of the material is less than 3×10^6 dynes/cm² (1 Hz, 25 °C), the material is considered a tacky PSA. Figure 9.13 shows the dynamic mechanical spectrum of a base elastomer and a tackified elastomer to demonstrate that the modulus of the elastomer changes upon addition of a tackifier.

As further evidence that a tackifier is needed to form a pressure-sensitive adhesive from an A-B-A triblock copolymer, Applicants submit a copy of the following

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journal article: C. D. Han et al., *J. Adhesion*, 28, pp. 201-230 (1989). The second paragraph of the introduction section states that "[s]ince the elastomer alone is insufficient to give rise to the desired level of adhesion and tack, one usually adds low molecular weight hydrocarbons (e.g., aliphatic or aromatic hydrocarbons, polyterpenes, rosin and its derivatives), in order to improve its ability to wet the surface sufficiently and to form a bond of measurable strength upon contracting. This low molecular weight material is referred to as a "tackifying resin." Tackifying resins come in a variety of chemical structures and physical properties. They are thermoplastics and usually form an amorphous glass at room temperature."

As yet further evidence that a tackifier is needed to form a pressure-sensitive adhesive from an A-B-A triblock copolymer, Applicants submit a copy of the following journal article: G. Kraus et al., *J. Adhesion*, 10, pp. 221-236 (1979). The introduction section confirms that a tackifying resin is added to a block copolymer to make it tacky.

Still further evidence that a tackifier is needed to form a pressure-sensitive adhesive from an A-B-A triblock copolymer is provided in the form of a copy of the following journal article: J. Kim et al., *J. Polymer Science: Part B: Polymer Physics*, 26, pp. 677-701 (1988). The introduction section states that various types of elastomers are used in pressure-sensitive adhesives. The first full paragraph of page 678 provides that "[i]n the use of these block copolymers as adhesives, one usually adds low molecular weight resin (e.g., aliphatic or aromatic hydrocarbons and polyterpenes) in order to improve its ability to wet the substrate surfaces sufficiently and to form a bond of measurable strength upon contact, since the block copolymer alone does not possess the sufficient tack needed for the desired adhesion. This low molecular weight material is referred to as a "tackifying resin." Choosing the proper block copolymer and tackifying resin is one of the most important tasks in developing successful adhesives, which meet with the required performance, as determined by tack and the resistance to peel and shear."

Regarding the references cited by the Examiner for the proposition that A-B-A triblock copolymers are pressure-sensitive adhesives, Applicants agree that these materials are often used to form a pressure-sensitive adhesive but these materials are not a pressure-sensitive adhesive without the addition of another material such as a tackifier to the formulation. The references submitted with these remarks provide

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evidence that A-B-A triblock copolymers are not inherently a pressure-sensitive adhesive.

Regarding paragraph 6 of the Advisory Action, the Examiner states that Applicants' arguments with respect to claims 7, 8, and 9 are moot in view of the fact that the triblock copolymer inherently encompasses a pressure-sensitive adhesive.

Applicants submit that the arguments in the last Response regarding these claims are not moot because the triblock copolymer is not inherently a pressure-sensitive adhesive. To the contrary, the *Handbook of Pressure-Sensitive Adhesives* expressly states that such materials have little inherent tack. The other provided references provide further supporting evidence that a tackifier is needed to convert the triblock copolymer to a pressure-sensitive adhesive.

Regarding paragraph 7 of the Advisory Action, the Examiner stated again that Attorney statements regarding the smoothness of the foam surface are not evidence. Applicants submit that any statement that be expressly or impliedly supported by the specification of the present invention or by the cited references do not require an affidavit or declaration.

Regarding paragraph 8 of the Advisory Action, Applicants note that the claims in question depend on claims that are non-obvious. Therefore, these claims are non-obvious at least based on this point.

Applicants submit that the pending claims are in condition for allowance.

Respectfully submitted,

September 10, 2003

Date

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Adhesion and Adhesives Technology

An Introduction

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Nick and Amanda*

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The Chemistry and Physical Properties of Elastomer-Based Adhesives

1 Introduction

the classes of adhesives, elastomer-based adhesives are probably the most familiar to the consumer. Many of the baby boom generation remember solvent-thinned, rubber-based paper adhesives used for elementary school projects. Many of the uses of furniture we have in our homes and offices are laminated wood. The active need for laminations is most often based on an elastomer. Probably the most widely recognized elastomer-based adhesive is coated on a backing and used as a pressure sensitive adhesive tape. In this chapter, the chemistry and physical properties of pressure-sensitive adhesives as well as other types of elastomer-based adhesives is discussed. The physical properties of pressure-sensitive adhesives is examined as these demonstrate many of the concepts discussed in this book. Other elastomer-based adhesives are discussed in terms of their chemistry, because fundamental information on these materials is limited.

The objectives of this chapter include the development of an understanding of chemistry of elastomer-based adhesives. Knowledge of the parameters necessary to formulate this type of adhesive and an appreciation of the test methods evaluating elastomer-based adhesives should be gained. Most important is the discussion on the dynamic mechanical properties of pressure-sensitive adhesives are related to the mechanism of action.

Pressure-Sensitive Adhesives

Pressure-Sensitive Tape Council [1] has defined pressure-sensitive adhesives as solids with the following properties:

- Aggressive and permanent tack
- Adheres with no more than finger pressure
- Requires no activation by any energy source
- Has sufficient ability to hold onto the adherend
- Has enough cohesive strength to be able to be removed cleanly from the adherend

The above definition of a pressure-sensitive adhesive (PSA) includes some concepts yet to be discussed but that are extremely important for this class of materials. The property we first notice about PSAs is their tack. We know what tack feels like but how do we describe it and, for that matter, how do we generate materials with tack? Tack is generated by adding certain low molecular weight materials to elastomers in a process called *tackification*. These *tackifiers*, because of their low molecular weight, decrease the cohesive strength of the elastomer. However, a PSA must have tack and sufficient cohesive strength to hold two things together. In this section, we see how a balance of properties is generated so that a PSA combines these seemingly mutually exclusive properties to yield a material with "sufficient ability to hold onto the adherend" as well as "be cleanly removed from the adherend."

For the most part, PSAs are used in coated form as the adhesives in pressure-sensitive adhesive tapes (PSATs). There is substantial technology associated with the manufacture of pressure-sensitive tapes but much of the information regarding PSATs is proprietary to those companies which manufacture them. The information about manufacturing does not yield more understanding as to how these materials perform and therefore, it is not discussed in this book.

9.2.1 Chemistry of the Base Resins Used in PSAs

A large variety of elastomers have been used as PSAs. The first material to gain widespread use was a natural rubber-based adhesive. Natural rubber is poly(isoprene) and is obtained from the *Hevea* rubber plant as a natural latex. The structure of poly(isoprene) is shown in Fig. 9.1. The latex is coagulated and then the rubber is usually smoked to eliminate bacteria and fungi which can degrade the rubber before it can be processed. The PSA manufacturer receives the natural rubber as a slab of smoked material which is often worked mechanically to reduce its molecular weight. The mechanically worked rubber is then dissolved in an appropriate solvent, mixed with the tackifier and coated or otherwise packaged. Natural rubber-based PSAs are still used in a number of PSAT applications including masking tape where they exhibit excellent removability after painting and baking. One of the primary attributes of natural rubber-based PSAs is their low cost, but they also are used extensively because of their high peel strength when properly formulated. The properties of natural rubber-based PSA lead to most of the discussion on PSA performance, which follows in a later section.

Natural rubber-based PSAs were the basis for all of the early PSA products. However, these adhesives had one primary flaw. Because of unsaturation in the backbone of the base polymer, the adhesive had a noticeable tendency to yellow and to crosslink, thus becoming brittle. The problem could in some ways be ameliorated by the addition of antioxidants, but, in general, natural rubber-based PSAs were unsuitable to long term exposure to the environment. This problem led to the introduction of a number of new base resins which did not suffer from these deficiencies.

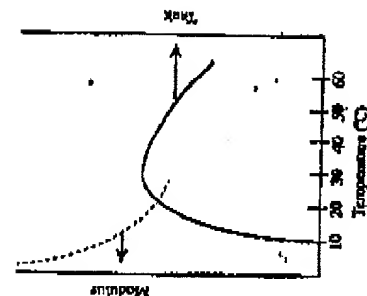


Figure 9.11 Plot of the tack and modulus measured at a rate of 1 Hz for a rubber-resin adhesive. Note that the tack reaches a maximum when the modulus drops below a certain level. The modulus value which corresponds to the onset of a high tack is known as the Dahlquist criterion.

is maximized near room temperature (this is done by formulation). Third, tack falls slowly as the temperature is increased.

Examine the modulus (dashed line) of the adhesive as a function of temperature using a rate of application of stress similar to the rate of the probe tack experiment in Fig. 9.11. The modulus of this rubber resin adhesive decreases rather dramatically as a function of temperature. In fact, as the temperature nears room temperature (the point at which the probe tack increases to a maximum), the modulus decreases to less than 3×10^6 dynes/cm². (Figure 9.11, which is only for demonstration, does not have units other than temperature.) In fact, it is found that the room temperature modulus of any tacky adhesive is less than 3×10^6 dynes/cm² when measured at a frequency of about 1 Hz. This finding is a criterion for tack and has been given the name "Dahlquist criterion for tack" after the scientist who studied this phenomenon [4].

Figure 9.10 showed that the way in which tack is obtained in a PSA is through the addition of a tackifying resin to an elastomer. As the resin concentration in the elastomer is increased, various practical adhesion properties change. Figure 9.12 shows a schematic of the modulus of a natural rubber/resin PSA as a function of the frequency of measurement and of the resin content. The dotted line shows the variation in modulus with frequency. The modulus curve is flat and is also above the Dahlquist criterion. As tackifier is added, the modulus decreases and at the frequencies in the graph, the second curve goes below the Dahlquist tack criterion. If the peel resistance of this PSA were measured, it would be relatively low. If we increase to another level of tackifier, we would find that now the modulus at low frequency was much below the tack criterion and the modulus at high frequency was now increased measurably. If the peel strength of this PSA is measured, it would be

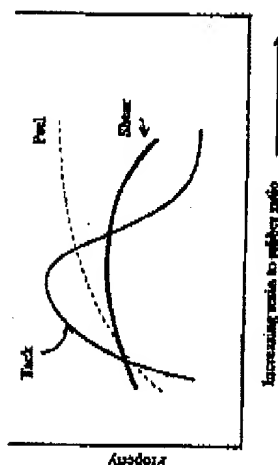


Figure 9.10 Diagram of the relationship of performance properties to the rubber-to-resin ratio in a natural rubber-based PSA. Note that the highest value of each performance property is not aimed at the same rubber-to-resin ratio. Optimum performance of a PSA is obtained with the balance of properties which meet the customer's expectations (adapted from Siles).

and or more. When a PSA is removed, the timescale is much shorter. Typical peel measurements are usually done on the order of inches per minute which, when looked at from the point of view of the adhesive, is on the order of tenths of a second. Therefore, a PSA is expected to behave as a liquid for timescales of seconds longer and to behave as a solid for timescales of tenths of seconds or less. At any higher temperature, these are properties which a viscoelastic material can achieve. A formulation of PSAs is the attainment of viscoelastic properties which allow the liquid-like properties at long timescales and peel (solid-like properties) at short timescales at the temperature of use.

9.6 PSA Viscoelasticity and Tack

It is the instantaneous wetting of a substrate under little or no applied pressure rapidly develop a measurable strength. Since tack requires the adhesive to act as a solid, it might be expected that if the adhesive becomes too stiff (too high a modulus), then the adhesive does not display tack. This phenomenon was studied in detail for rubber-resin adhesives. It is that work which forms the basis for this discussion.

The variation of probe tack with temperature is one key to understanding which property of materials leads to the phenomenon of tack. This discussion above indicates that the timescale of the probe tack test is important. Figure 9.11 represents the measurement of probe tack as a function of temperature when the measurement is taken at a withdrawal rate of a few centimeters per second and a contact time on the order of a second.

There are several important features in Fig. 9.11. First, probe tack goes rapidly zero as the temperature falls even slightly below room temperature. Second, tack

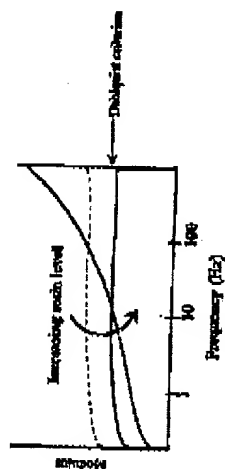


Fig. 9.12 Plot of modulus of a pressure sensitive formulation as a function of frequency at three resin levels in the adhesive

nd that it had now increased to a substantial value. Understanding this phenomenon is key to understanding the tack and peel performance.

Another way of examining this phenomenon is to plot of the shear modulus of a base elastomer as a function of temperature measured at about 1 Hz as well as that of the tackified base elastomer, as shown in Fig. 9.13. This type of data is similar to the dynamic mechanical data presented in Chapter 5. The base elastomer is shown as the dashed line. The glass transition temperature, when measured at 1 Hz, is somewhat below room temperature. The dynamic mechanical determination of shear storage modulus of the tackified adhesive is shown as the solid line in Fig. 9.13. The very interesting effect of having the tackifier act as an anti-plasticizer, it is, increasing the T_g of the tackified adhesive is seen. Above the T_g , however, plastic modulus is decreased. It is indicated that the storage modulus has increased below that required by the Dahlquist criterion.

The time-temperature superposition principle states that the effects of time and pressure on a viscoelastic material are inversely related. Therefore, when the same physical properties as shown in Fig. 9.13 are measured at a higher frequency, one might expect to obtain the plot shown in Fig. 9.14. When measured at 100 Hz, it is

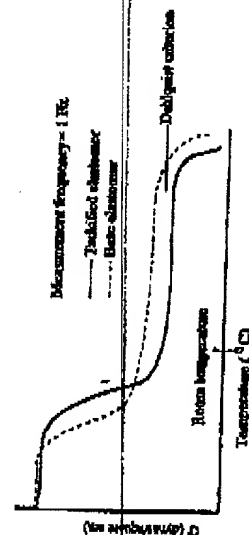


Fig. 9.13 Dynamic mechanical spectrum of a PSA-based elastomer in the tackified and untackified state. The measurement is done at a single frequency but as a function of temperature. Note that the tackified elastomer has a glass transition below that of the Dahlquist criterion

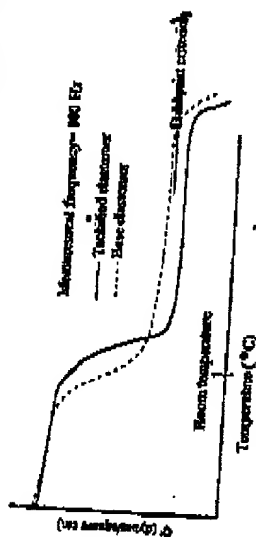


Fig. 9.14 Plot of the shear modulus of a PSA elastomer with and without tackification measured as a function of temperature but at a frequency of 100 Hz. Note that the curves have shifted towards higher temperatures as the frequency was increased

seen that the entire dynamic mechanical spectrum of the shear storage modulus of the adhesive has shifted to higher temperatures. The T_g of the tackified adhesive is now above room temperature. This adhesive would be expected to exhibit greater stiffness and thus provide some physical strength when the tape is tested.

The above discussion implies that the resin must be completely miscible with the base elastomer. Indeed, if the resin were not soluble, one would not expect a change in the physical properties of the base elastomer. Instead, two glass transition temperatures, with no change in the T_g of the base elastomer, would be expected. In systems where two materials of substantially differing T_g s are mixed and these materials are soluble in one another, the overall glass transition temperature of the solid solution can often be predicted by the Fox equation [5]:

$$\frac{1}{T_g} = \sum_i \phi_i \frac{1}{T_{gi}}$$

where the ϕ_i is the weight fraction of the i th soluble component in the mixture and T_{gi} is the glass transition temperature of the i th soluble component. The Fox equation can often be used to predict the T_g of elastomer/elastomer solid solutions and in fact, can show that components are not soluble in one another.

If the elastomer and the tackifier are not soluble in one another, what sort of physical situation might be expected? In the case of normal polymer solutions, several results could occur. One possibility is gross separation of the two phases, particularly when the interfacial tension between the components is large. When the incompatibility and the interfacial tension are not that large, microscopic phase separation occurs similar to that discussed in Chapter 8 on toughening phase. In this situation two T_g s are exhibited. In a particularly sinister situation, the resin could phase separate into microscopic phases, and by surface tension effects, phase separate into a solid layer at the surface of the PSA. Since the resin is glassy, it would not exhibit tack and the PSA would not perform as expected. Therefore, care must be taken to choose tackifiers that are completely soluble in the elastomer to be tackified.

4 The Chemistry and Physical Properties of Elastomer-Based Adhesives

After a certain time after application, has enough cohesive strength and *knitting ability* that two surfaces coated with the adhesive have *green strength* immediately after they are mated. *Knitting ability* is an autohesion phenomenon in which elastomer elastomer molecules are mobile enough to quickly form a bond (likely through interdiffusion) immediately after contact with little or no applied pressure. Few elastomers have this ability. *Green strength* indicates that the adhesive bond is strong enough to be handled a short time after the elastomers are mated but much before full cure is obtained. One can imagine the utility of such an adhesive in mass production operations where it is much less expensive to store a part during cure as to slow down the production line to allow the adhesive time to set up. The choice of solvent in such an adhesive system is critical. A combination of solvents is usually chosen with a rapidly evaporating solvent as the primary carrier and a slower evaporating solvent to provide tack during bonding.

Because of increasing regulation on the use of organic solvents, the use of latex-based adhesives has increased markedly. Such systems, however, often have problems due to slow evaporation of water, less tack, and microbial buildup in the wet adhesive. For such systems to be useful in production lines, infrared heaters or ovens are often used to aid in the evaporation of the solvent. In addition, wetting agents or other polymeric substrates are often problematic when latex-based RBAs are used. Often a small amount of solvent, called a *condensing aide* which is soluble both in the elastomer and water, is added to latex systems to aid in wetting as well as to improve the coalescence of the latex particles. A recent improvement in the ability of latex-based RBAs has come with the development of a new application method. A salt solution is spray-applied simultaneously with the latex RBA, the salt is destabilized during the operation and it coagulates almost immediately upon application with the expulsion of water. This improves the drying production line speeds where latex based adhesives are used.

4 Summary

Elastomer-based adhesives come in two primary forms, the pressure-sensitive adhesive (PSA) and the rubber-based adhesive (RBA). The formulation of these two types of adhesives are quite similar in that a base elastomer provides much of the performance, which is modified by the addition of tackifiers and crosslinking agents. A primary difference between the two materials is that the PSA is dry and ready to use in its commercial form while the RBA usually comes in a carrier (solvent or latex) which must be removed before the bond can be effected. The ultimate bonding strength of the PSA is substantially less than that of an RBA, which should be considered semi-structural in character. The performance properties of a PSA were assessed in detail, especially as they related to dynamic mechanical properties. In particular, the properties of tack and peel were related to dynamic mechanical properties.

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Viscoelastic Behavior and Order-Disorder Transition in Mixtures of a Block Copolymer and a Midblock-associating Resin

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Synopsis

The viscoelastic behavior and order-disorder transition in mixtures of a block copolymer and a midblock-associating resin were investigated. The block copolymers investigated were polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS) copolymers (Shell Development Company), specifically Kraton D-4107, with the block molecular weights 10,000-120,000-10,000, and Kraton U-1111, with the block molecular weights 15,000-100,000-15,000. The midblock-associating resin investigated was a resin polymerized from C_6 hydrocarbons, referred to as Floctac 958HT (Hercules Inc.), which is an aliphatic hydrocarbon containing considerable amounts of cyclic structures, with a weight-average molecular weight of 1,100 and a glass transition temperature T_g of 49°C. In the investigation, mixtures of the block copolymer and Floctac 958HT were prepared with toluene as solvent. Temperature scans of the samples were made to obtain information on dynamic storage modulus G' , dynamic loss modulus G'' , and loss tangent $\tan \delta$, using a Rheometric dynamic mechanical spectrometer. It was found that Floctac 958HT decreased the plateau modulus G'_p and increased the T_g of the polystyrene midblock of the SIS block copolymer in the mixtures. This experimental observation led to the conclusion that Floctac 958HT associates (or is compatible) with the rubbery polyisoprene midblock of the SIS block copolymer. The order-disorder transition behavior of mixtures of SIS block copolymer and Floctac 958HT was also investigated by a rheological technique proposed by Han and Kim (Rheol. Acta 39, 1900, 1999). The order-disorder transition temperature T_{ODT} (i.e., the temperature at which the ordered microdomain structure of the block copolymer completely disappears) of the SIS block copolymer decreased steadily with increasing amount of Floctac 958HT in the mixture. With the information determined on T_g , a phase diagram for the mixtures was constructed, showing the boundary between the homogeneous and inhomogeneous phase in the mixtures. The phase diagram is in qualitative agreement with the theoretical predictions of Vilevsky and Neelakanti (Sci. 29).

INTRODUCTION

Various types of elastomers are used in the pressure-sensitive and hot-melt adhesive industry. Although natural rubber still has the largest volume, adhesives based on synthetic elastomers have grown steadily in recent years. Among the many synthetic elastomers commercially available, polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS) and polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) triblock copolymers are widely used for pressure-sensitive and hot-melt adhesives. The usefulness of these block copolymers as adhesives is a direct consequence of their unique structure. The

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polystyrene endblock, which is incompatible with the polydiene midblock, separates on a microscopic scale to form polystyrene domains, thereby creating a physically crosslinked network structure.

In the use of these block copolymers as adhesives, one usually adds low molecular weight resin (e.g., aliphatic or aromatic hydrocarbons and polyterpenes) in order to improve its ability to wet the substrate surfaces sufficiently and to form a bond of measurable strength upon contact, since the block copolymer alone does not possess the sufficient tack needed for the desired adhesion. This low molecular weight material is referred to as a "tackifying resin." Choosing the proper block copolymer and tackifying resin is one of the most important tasks in developing successful adhesives, which meet with the required performance, as determined by tack and the resistance to peel and shear.

Tack is essentially a measure of viscous flow under conditions of high strain rates and low stress levels, whereas shear adhesion is a measure of viscous flow at low strain rates and intermediate stress levels. The principal problem involved in the application of adhesives to substrates is rheological in nature. In order to have good tack, the viscosity of the block copolymer/resin mixture must be lower than that of the block copolymer itself, so that it flows easily and wets the surface sufficiently upon application. This requires a relatively low modulus of adhesion, as well as a short relaxation time to relieve internal stresses. On the other hand, viscoelasticity information is required to understand the ultimate properties of an adhesive. Since tack, shear adhesion, and peel strength are determined at different strain rates or stresses, the viscoelasticity must be well understood.

When formulating an adhesive with an ABA-type block copolymer, a distinction must be made between the effect of midblock-associating resin and that of endblock-associating resin. The primary function of a midblock-associating resin is to develop tack in the block copolymer/resin mixture, whereas the primary function of an endblock-associating resin is to impart reinforcement to the polystyrene endblock. It is believed that in order to develop tack in the mixture of a block copolymer and a low molecular weight resin, the resin must be compatible with the block copolymer. If the resin is not compatible with the block copolymer, it will form a separate phase, making the mixture undesirable as a pressure-sensitive adhesive. It can then be surmised that a better understanding of the viscoelastic behavior and thermodynamic compatibility of mixtures of an SIS (or SBS) block copolymer and a midblock-associating resin is of fundamental and technological importance to the pressure-sensitive and hot-melt adhesive industry.

In this paper we will report on our recent investigation of the viscoelastic behavior and order-disorder transition in mixtures of block copolymer and midblock-associating resin.

PREVIOUS STUDIES

Rheological Behavior of Mixtures of a Block Copolymer and a Homopolymer

Kraus and coworkers¹⁻³ reported on a series of experimental studies of the viscoelastic properties of polystyrene-block-polydiene copolymers and mix-

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tures of these block copolymers with a midblock-associating resin (i.e., tackifying resin). They reported that the use of a tackifying resin increased the glass transition temperature T_g of the polydiene midblock and decreased the dynamic storage modulus G' in the plateau region, often referred to as the plateau modulus G_N^0 . Tackifying resins have molecular weights in the range 1,000–3,000 and thus may be thought of as diluents with regard to mixtures with block copolymer.

According to the classical theory of rubber elasticity,⁴ G_N^0 for dilute polymer solutions is proportional to the square of the volume fraction of the polymer, ϕ_2 ,

$$G_N^0 = \frac{1}{2} G_N^0 \quad (1)$$

where G_N^0 is the plateau modulus of the polymer. Note that G_N^0 is related to the molecular weight of entanglement spacing M_e :

$$G_N^0 = \rho RT / M_e \quad (2)$$

where ρ is the density, R is the universal gas constant, and T is the absolute temperature. Assuming that the polystyrene domains in the block copolymer may be regarded as filler dispersed in a continuous polydiene matrix, Holden⁵ estimated G_N^0 for ABA-type block copolymers using the following expression:⁴

$$G_N^0 = (\rho RT / M_e) \{ 1 + 2.5C + 14.1C^2 \} \quad (3)$$

where C is the concentration of filler, which in this case is the concentration of polystyrene domains in the block copolymer.

When a midblock-associating resin is added to a block copolymer, often one cannot observe a clear plateau region in plots of G' versus temperature. Kraus and Rollmann¹ suggested that in such situations G_N^0 of a mixture consisting of a block copolymer and a midblock-associating resin be approximated by the G' value at the minimum value of loss tangent ($\tan \delta_{\min}$) and that values of G_N^0 for such mixtures be estimated by combining eqs. (1) and (3), i.e.,

$$G_N^0 = G'(\tan \delta_{\min}) = \frac{1}{2} (\rho RT / M_e) \{ 1 + 2.5C + 14.1C^2 \} \quad (4)$$

where ϕ_2 is the volume fraction of the polymer in the polydiene phase alone, and C is the volume fraction of polystyrene block in the entire composition. It should be pointed out that eq. (4) assumes that the entire amount of the tackifying resin added has entered (or associated with) the polydiene phase of the block copolymer.

It should be noted that scaling law interpretations by de Gennes⁶ suggest that G_N^0 for a dilute polymer solution should be proportional to the 2.35 power of the polymer volume fraction. Raju et al.⁷ reported some results of the viscoelastic behavior of polybutadiene, polyisoprene, and hydrogenated polybutadiene in various diluents and obtained the relation

$$G_N^0 \propto \phi_2^2 \quad (5)$$

where $2.0 \leq \alpha \leq 2.3$, essentially confirming the theoretical prediction of de Gennes.

Recently, Glass and Chu³ studied the viscoelastic properties of mixtures of natural rubber (or a synthetic elastomer) with a tackifying resin. They reported that (1) the molecular weight of the tackifying resin is very important for controlling the compatibility of mixtures, and phase separation was observed as the molecular weight of the tackifying resin was increased; (2) the T_g of compatible mixtures of an elastomer and a tackifying resin, as determined by the peak value of $\tan \delta$, can be estimated by the Fox equation¹⁰

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \quad (6)$$

where T_{g1} , T_{g2} , and T_g are the peak temperatures of $\tan \delta$ for the mixture and the constituent components, respectively, and w_1 and w_2 are the weight fractions of the constituent components; and (3) the plateau modulus for mixtures of a block copolymer and a tackifying resin is predicted reasonably well by de Gennes' theory.⁷

Order-Disorder Transition in Block Copolymer and Its Mixtures with a Homopolymer

It is well established that when polystyrene-*block*-polybutadiene (SB), polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS), or polystyrene-*block*-polybutadiene-*block*-polystyrene (SIS) copolymer is heated above the upper polystyrene-*block*-polystyrene (SIS) copolymer is heated above the upper polystyrene (PS) domains will eventually be destroyed, and then the block copolymer will form a homogeneous phase. The critical temperature at which the PS domains are completely destroyed is often referred to as the "order-disorder transition temperature" T^* .

In recent years, Leibler¹¹ has developed a theory that predicts the T_g of block copolymers and suggested that a light (x-ray) scattering technique be used to measure T^* . Indeed, Hsiao¹² and coworkers¹³⁻¹⁵ and Roe and coworkers¹⁶⁻¹⁸ have investigated experimentally the order-disorder transition behavior of SB and SBS block copolymers and determined the T_g 's using small-angle x-ray scattering (SAXS). They reported that the scattered intensity, which is related to the ordered microdomain structure, persists well above the glass transition temperature of the PS domains but disappears at a critical temperature T^* where the block copolymer becomes a homogeneous melt. For instance, using an SB diblock copolymer, Roe and Zil¹⁶ have reported that the order-disorder transition continued over the temperature range from 80 to 140°C, which indicates that T^* for the particular SB block copolymer was 140°C. They obtained similar results for an SBS triblock copolymer. Kress and Hsiao¹⁷ conducted an experimental SAXS study on an adhesive system and observed that the adhesive showed the same scattering pattern as the block copolymer and that the T_g of the adhesive was lower than that of the block copolymer.

Although SAXS is precise experimental technique, it requires laborious data analysis to extract information on the T_g of a block copolymer or its mixtures with tackifying resin. Very recently, Han and Kim¹⁹ have proposed a rheological technique to determine the T_g of a block copolymer, using the dynamic viscoelastic properties measured under isothermal conditions. Rati-

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cally, the technique calls for logarithmic plots of dynamic storage modulus G' versus dynamic loss modulus G'' , whereby the T_g of a block copolymer is determined by the temperature at which $\log G'$ versus $\log G''$ plots cease to vary with temperature. Earlier, Han and coworkers²⁰⁻²² showed that when the morphological state of a polymer (a homopolymer, graft copolymer, or heterogeneous polymer blend), does not vary with temperature, then $\log G'$ versus $\log G''$ plots become virtually independent of temperature.

Noelani and coworkers^{23,24} have developed a theory of phase equilibria in mixtures of a block copolymer and a homopolymer, using functional integral formalism, and presented phase diagrams for the mixtures. In the development of the theory, they considered situations where the homopolymer added has the same chemical structure as one of the blocks in the block copolymer and the PS domains in the block copolymer have lamellar structure. Their predictions suggest that the T_g of a mixture of block copolymer and homopolymer can be higher or lower than the T_g of the block copolymer itself, depending on the ratio of the molecular weight of the homopolymer added to that of a block in the block copolymer.

Roe and Zil¹⁶ reported that the addition of polybutadiene (PB) homopolymer ($M_w = 26,000$) to an SB diblock copolymer ($M_w = 28,000$) decreased the T_g of the block copolymer, as determined by the SAXS technique. They also constructed a phase diagram for the SB block copolymer/PB homopolymer mixture using both light scattering and SAXS. They found the theoretical predictions of Noelani and coworkers²³ to be in general agreement with their experimental results.

EXPERIMENTAL

Materials

The block copolymers investigated in this study were two different grades of SIS triblock copolymer, specifically Kraton D-1107[®] and Kraton D-1111[®] (Shell Development Company). Table I gives the molecular characteristics of the block copolymers investigated. The midblock-associating resin investigated was a resin polymerized from C_{60} hydrocarbon, referred to as Picoctac 98BHT[®] (Hercules Inc.). This resin is widely used as a tackifying resin in the formulation of pressure-sensitive adhesives. In the present investigation, an attempt was made to elucidate the structure of Picoctac 98BHT, using infrared spectroscopy and ¹H nuclear magnetic resonance spectroscopy. We have confirmed that Picoctac 98BHT is an aliphatic hydrocarbon containing considerable amounts of cyclic structures but no aromatic structures. Using gel permeation chromatography, we determined the weight-average molecular

TABLE I
Molecular Characteristics of the Block Copolymers Employed

Sample code	Structure	Molecular weight ($\times 10^{-3}$)	Styrene (wt%)	Triblock/ diblock ratio
Kraton D-1107	SIS	105-1266-185	15	80:20
Kraton D-1111	SIS	158-1973-258	20	90:10

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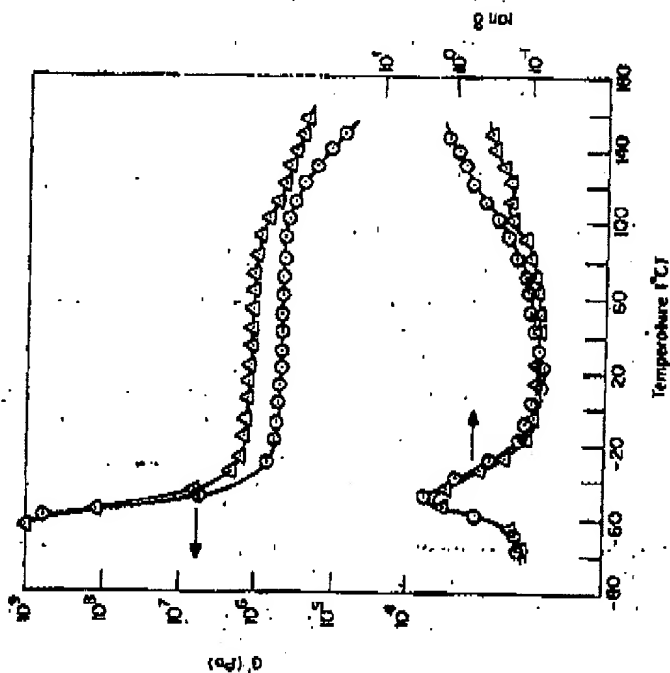


Fig. 1. Log G' and $\tan \delta$ versus temperature: (O) Kraton 1107, (Δ) Kraton 1111.

RESULTS

Viscoelastic Behavior of Mixtures of an SIS Block Copolymer and a Midblock-associating Resin

Figure 1 gives plots of G' and $\tan \delta$ as functions of temperature for Kraton 1107 and Kraton 1111. The following observations are worth noting in Figure 1: (1) both Kraton 1107 and Kraton 1111 exhibit a well-defined plateau modulus G_N' that extends from about -30 to 70°C, where the value of G_N' for Kraton 1111 is larger than that of Kraton 1107. This can be attributed to the fact that Kraton 1111 has more polybutyrene domains than Kraton 1107 (see Table I); (2) a sharp peak in $\tan \delta$ at about -50°C representing the T_g of the polybutyrene midblock is seen in both Kraton 1107 and Kraton 1111; and (3) a peak in $\tan \delta$ at about 160°C representing the polybutyrene endblock is seen in Kraton 1111 but not in Kraton 1107. The apparent absence of a $\tan \delta$ peak at a higher transition region for Kraton 1107 is due to the fact that it contains an insufficient amount of polybutyrene domains, compared with that in Kraton 1111 (see Table I).

Figure 2 gives plots of G' and $\tan \delta$ as functions of temperature for mixtures of Kraton 1107 and Picozac 93BHT, and Figure 3 gives similar results for mixtures of Kraton 1111 and Picozac 93BHT. It is seen in Figures 2 and 3 that as the amount of Picozac 93BHT increased, the plateau modulus of the

TABLE II
Formulations Employed for Mixtures of Block Copolymer and Midblock-Associating Resin

	1	2	3	4	5	6	7	8
Kraton D-1107	100	70	50	30				
Kraton D-1111					100	70	50	30
Picozac 93BHT		30	50	70		30	50	70
T_g (°C)	-50	-31	0	32	-50	-28	0	36
$G_N' \times 10^{-4}$ (Pa)	4.0	1.5	0.36	0.35	10.5	2.4	1.1	0.59

Note: All formulations are on a weight basis.

weight (M_w) of Picozac 93BHT to be 1100, with a polydispersity of 1.7. The glass transition temperature of Picozac 93BHT was found to be 43°C, which was determined using a duPont differential scanning calorimeter (DSC) with a heating rate of 10°C/min.

Sample Preparation

Samples for viscoelastic measurements were prepared by first dissolving a predetermined amount of block copolymer and tachifying resin in toluene (10 wt% solid in solution) in the presence of an antioxidant (Irganox 1010, Ciba-Geigy Group) and then slowly evaporating the solvent. The evaporation of solvent was carried out initially in open air at room temperature for a week and then in a vacuum oven at 40°C for 3 days. The last trace of solvent was removed by drying the samples in a vacuum oven at an elevated temperature by gradually raising the oven temperature up to 110°C. The drying of the samples was continued until there was no further change in weight. Finally, the samples were annealed at 130°C for 10 h. The formulations employed in this investigation are given in Table II.

Measurement of Dynamic Viscoelastic Properties

A dynamic mechanical spectrometer (Rheometrics Inc.) in the parallel plate mode (8 mm diameter plates with a 2 mm gap) was used to take temperature scans of block copolymer and its mixtures with Picozac 93BHT. With temperature scans from about -100 to 140°C at a fixed angular frequency of 10 rad/s, dynamic storage modulus G' , dynamic loss modulus G'' , and loss tangent $\tan \delta$, defined as G''/G' , were plotted. With the measurements, values of the plateau modulus G_N' were determined from the value of G' where $\tan \delta$ showed a minimum, $G'(\tan \delta_{\min})$.

A Model R16 Rheometer (Sengco Control Inc.) in the one-cent plate mode (25 mm diameter plate and 4° cone angle with a 0.16 mm gap) was used to measure G' and G'' as a function of angular frequency (ω) at various temperatures, for mixtures of Kraton D-1107 (or Kraton D-1111) with Picozac 93BHT. The purpose of this experiment was to investigate the effect of the midblock-associating resin (Picozac 93BHT in the present study) on the thermally induced order-disorder transition behavior of block copolymers (Kraton D-1107 and Kraton D-1111 in the present study) using $\log G' - \log G''$ plots.

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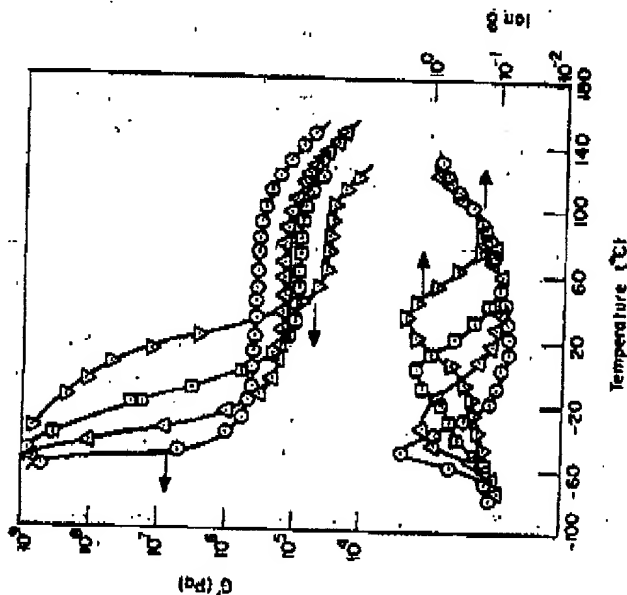


Fig. 2. Log G' and $\tan \delta$ versus temperature: (O) Kraton 1107, (Δ) Kraton 1107/Picoteac 95BHT = 70:30, (∇) Kraton 1107/Picoteac 95BHT = 50:50, (∇) Kraton 1107/Picoteac 95BHT = 30:70.

mixture decreased, and $\tan \delta$ shifted toward higher temperatures. This observation can be construed as indicating that over the concentration range investigated, Picoteac 95BHT associates (i.e., is compatible) with the rubbery polystyrene midblock in both Kraton 1107 and Kraton 1111. Our calculations indicate that there is reasonably good agreement between the values of G' that is determined at the minimum value of $\tan \delta$, i.e., $G'(\tan \delta_{\min})$ in Figures 2 and 3, and the value of G_N^* that is predicted by eq. (4) for both block copolymers, Kraton 1107 and Kraton 1111. The results are summarized in Table III.

Plots of $G'(\tan \delta_{\min})/(\rho RT)(1 + 2.5C + 14C^2)$ versus volume fraction of block copolymer ϕ_c were prepared for mixtures of Kraton 1107 and Picoteac 95BHT and mixtures of Kraton 1111 and Picoteac 95BHT. It has been found that the slope of the plots is about 2.1, which is in good agreement with the prediction by eq. (4) but slightly lower than the theoretically predicted value [i.e., the exponent $\alpha = 2.35$ in eq. (5)] by de Gennes.⁷ It should be mentioned that eq. (4) assumes that no interphase is present between the polystyrene (PT) chains and polystyrene (PS) domains in both Kraton 1107 and Kraton 1111. On the other hand, experimental evidence indicates that an interphase does exist between the PI phase and PS domains in an SIS block copolymer.²⁸⁻³²

We now consider the effect of Picoteac 95BHT on the temperature at which the peak of $\tan \delta$ occurs. It is seen in Figure 3 that the $\tan \delta$ peak in the upper

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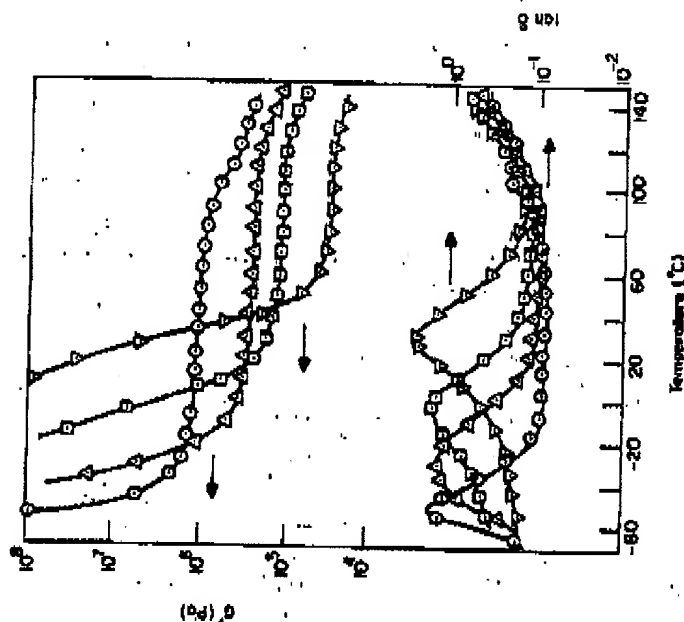


Fig. 2. Log G' and $\tan \delta$ versus temperature: (O) Kraton 1111, (Δ) Kraton 1111/Picoteac 95BHT = 70:30, (∇) Kraton 1111/Picoteac 95BHT = 60:40, (∇) Kraton 1111/Picoteac 95BHT = 30:70.

TABLE III
Comparison of the Plateau Modulus Obtained from $\tan \delta_{\min}$ with that Calculated from E_g (9) and Order-Disorder Transition Temperature (T_c)

Kraton/Picoteac by wt	$G'(\tan \delta_{\min})$ $\times 10^{-4}$ (Pa)	Calculated G_N^* $\times 10^{-4}$ (Pa)	T_c (°C)
Kraton 1107/Picoteac 95BHT Mixtures			
100:00	40.9	62.9	220
70:30	15.9	21.5	200
50:50	9.5	11.5	180
30:70	2.5	3.6	160
Kraton 1111/Picoteac 95BHT Mixtures			
100:00	102.0	96.9	> 260
70:30	24.9	30.5	> 240
50:50	11.8	12.5	230
30:70	2.5	2.7	200

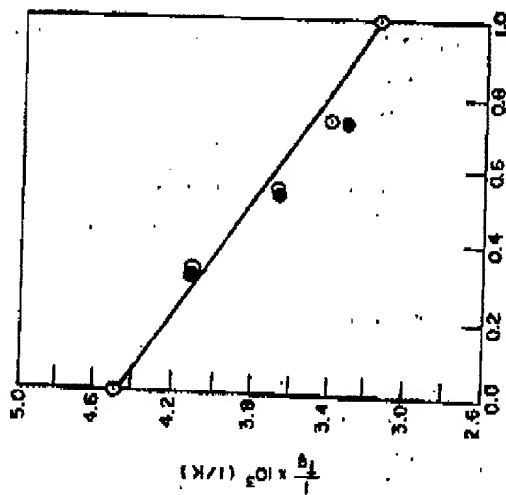


Fig. 1. $1/T_g$ versus weight fraction of Picrotac 96BHT: (○) Kraton 1107/Picrotac 96BHT mixtures; (□) Kraton 1111/Picrotac 96BHT mixtures.

transition region that was present in Kraton 1111 is absent in the mixtures of Kraton 1111 and Picrotac 96BHT. This is due to the fact that the weight fraction of polystyrene in the mixtures is decreased by the addition of midblock-associating resin, Picrotac 96BHT. In fact, the amount of polystyrene in the 70/30 Kraton 1111/Picrotac 96BHT mixture is about 16 wt%, which is almost the same as that in Kraton 1107. Note that Kraton 1107 does not exhibit a $\tan \delta$ peak in the upper transition region, as may be seen in Figure 2. However, as may be seen in Figures 2 and 3, the addition of Picrotac 96BHT to Kraton 1107 and Kraton 1111 increased the $\tan \delta$ peak in the lower transition region, which represents the rubbery polystyrene phase.

Figure 4 gives plots of the reciprocal of the absolute temperature at which the peak of $\tan \delta$ occurs (i.e., the reciprocal of the T_g of the mixture) against weight fraction w_1 of Picrotac 96BHT in the mixtures of Kraton 1111 and Picrotac 96BHT and in the mixtures of Kraton 1107 and Picrotac 96BHT. The solid line in Figure 4 represents the theoretical prediction by eq. (6). It is expected that there would be no difference in the T_g of the rubbery polystyrene phase between the Kraton 1107/Picrotac 96BHT mixtures and the Kraton 1111/Picrotac 96BHT mixtures, if the same amount of Picrotac 96BHT is added to each block copolymer and if the Picrotac 96BHT added is compatible with Kraton 1107 and Kraton 1111 at that particular composition. It is seen in Figure 4 that the experimentally determined values of T_g are in good agreement with those predicted by eq. (6) over the entire composition range investigated, although the agreement is not so good for the 30:70 Kraton 1107/Picrotac 96BHT and 30:70 Kraton 1111/Picrotac 96BHT mixtures.

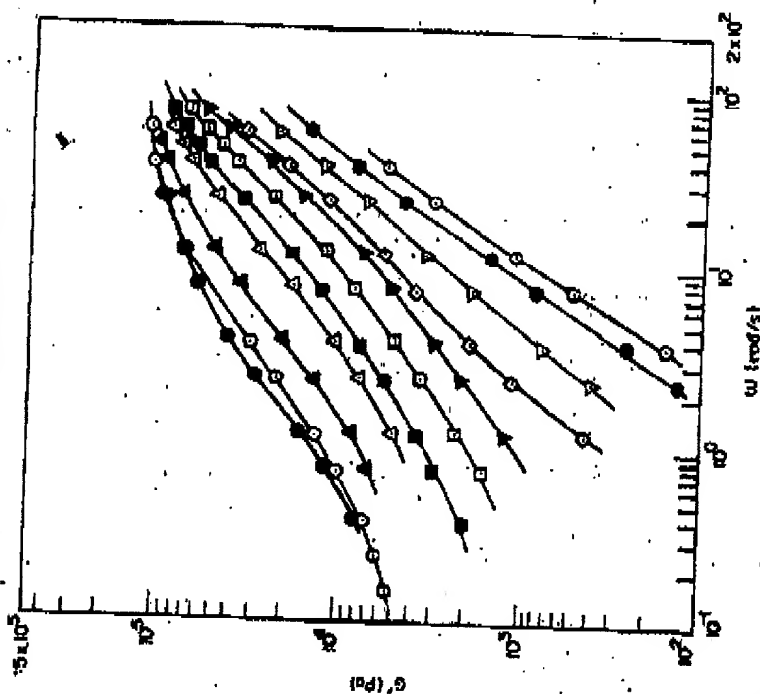


Fig. 5. $\log G'$ versus $\log \omega$ for Kraton 1107 at various temperatures ($^{\circ}\text{C}$): (○) 176, (△) 180, (□) 190, (◇) 200, (○) 210, (□) 220, (△) 230, (○) 240.

It can be concluded from the above observations on the plateau modulus and glass transition temperatures that Picrotac 96BHT is compatible with the polystyrene midblock of either Kraton 1107 or Kraton 1111 over the entire composition range investigated.

Order-Disorder Transitions Behavior of Mixtures of a Block Copolymer and a Midblock-Associating Resin

Let us examine the effect of Picrotac 96BHT on the order-disorder transition behavior of the block copolymers investigated using the rheological technique proposed by Han and Kim.² Figure 5 gives logarithmic plots of G' versus angular frequency ω , and Figure 6 gives logarithmic plots of G'' versus ω for Kraton 1107, which were measured at 11 different temperatures ranging from 140 to 240 $^{\circ}\text{C}$. It is seen in Figures 5 and 6 that values of G' and G'' decrease with increasing temperature, and in the low frequency range the slope of $\log G'$ versus $\log \omega$ increases with increasing temperature, whereas the slope of $\log G''$ versus $\log \omega$ remains almost constant as the temperature is increased. However, when $\log G'$ is plotted against $\log G''$, as given in Figure

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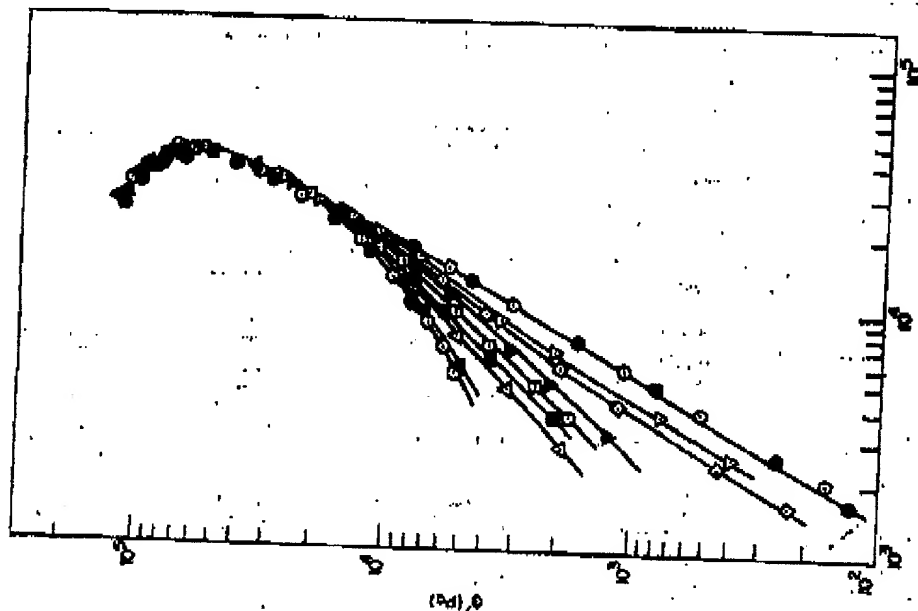


Fig. 7. Log G' versus log G'' for Kraton 1107 at various temperatures. Symbols are as in Figure 5.

the 50:50 and 30:70 Kraton 1107/Picoteac 96BHT mixtures. We have observed that T_g decreases as the concentration of Picoteac 96BHT in the mixture increases. Table III gives a summary of the values of T_g determined. It should be emphasized that a more precise value of T_g could have been obtained if rheological measurements had been taken at a smaller temperature interval than the 10°C used here. However, our objective was not to determine the precise value of T_g but to observe the effect of the concentration of Picoteac 96BHT in its mixtures with Kraton 1107 or Kraton 1111 on the T_g of the mixture.

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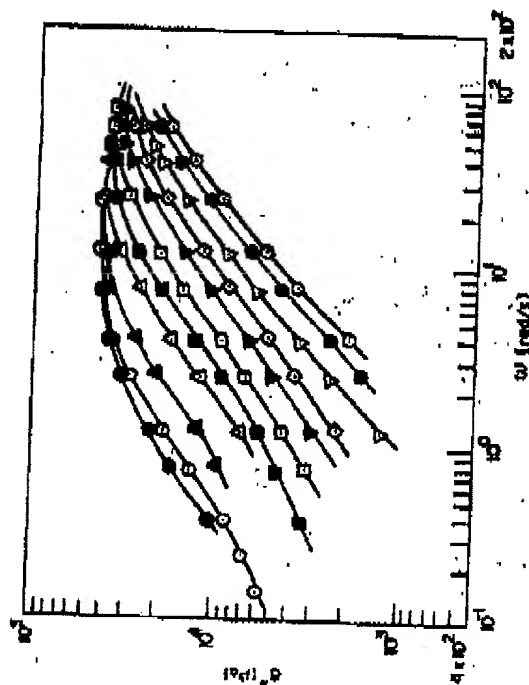


Fig. 8. Log G' versus log G'' for Kraton 1107 at various temperatures. Symbols are as in Figure 5.

7, G' for a fixed value of G'' decreases continuously with increasing temperature until it reaches 230°C. In other words, log G' versus log G'' plots become independent of temperature at 230°C and higher. Unfortunately, we were not able to take measurements at temperatures above 240°C owing to the thermal degradation of Kraton 1107.

In recent years, Han and coworkers²¹⁻²⁵ have demonstrated experimentally that plots of log G' versus log G'' become virtually independent of temperature for flexible homopolymers in the molten state (i.e., above their melting or glass transition temperatures), and for heterogeneous polymer systems (e.g., graft copolymers and incompatible polymer blends), as long as their morphological states do not vary with temperature in the range over which rheological measurements are taken. Very recently, Han and Jhon²⁶ offered a theoretical interpretation to the experimental observations made for flexible monodisperse homopolymers, using molecular theories.

On the basis of the theoretical and experimental investigations referred to above, we can conclude from Figure 7 that Kraton 1107 has achieved a disordered structure (i.e., a homogeneous phase) at temperatures 230°C and above. Therefore, we conclude that the order-disorder transition temperature T_g for Kraton 1107 is about 230°C.

Let us now examine how the addition of a midblock-associating resin, Picoteac 96BHT, affects the order-disorder transition temperature T_g of Kraton 1107. Figure 8 gives log G' versus log G'' plots for the 70:30 Kraton 1107/Picoteac 96BHT mixture. It is shown in Figure 8 that the T_g for the 70:30 Kraton 1107/Picoteac 96BHT mixture is about 230°C, which is about 30°C lower than the T_g of the Kraton 1107. Similar plots were prepared for

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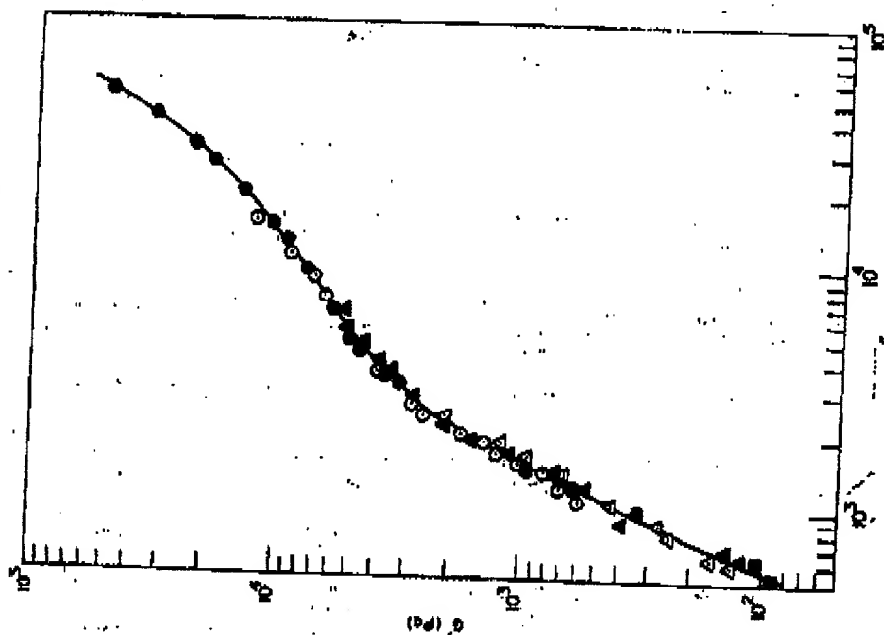


Fig. 3. Log G' versus log G'' for the 10:90 Kraton 1107/Flcoteac 95BHT mixture at various temperatures ($^{\circ}\text{C}$): (●) 120, (□) 140, (Δ) 160, (◊) 180.

characteristic of low molecular weight resins. At temperatures above 80 $^{\circ}\text{C}$, micelles may have formed, a phenomenon reported by Watanabe et al.²¹ and Raby and Buehler²² for mixtures with block copolymers prepared with organic solvents. It should be pointed out that the upper limit of the range of concentrations of block copolymers used by these investigators was much less than 10 wt% of block copolymer.

Figure 29 gives log G' versus log G'' plots for Kraton 1111 at 230, 240, and 260 $^{\circ}\text{C}$. It was not possible to take rheological measurements at temperatures above 260 $^{\circ}\text{C}$ owing to thermal degradation. On the other hand, Kraton 1111, which is much more viscous than Kraton 1107, did not permit us to take rheological measurements at temperatures below 200 $^{\circ}\text{C}$ either. Note that

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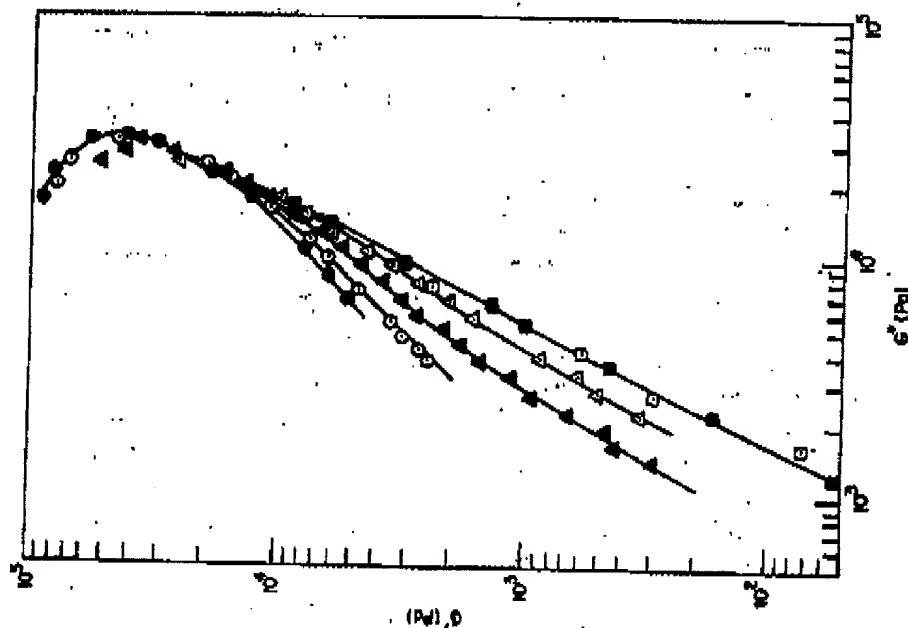


Fig. 4. Log G' versus log G'' for the 70:30 Kraton 1107/Flcoteac 95BHT mixture at various temperatures ($^{\circ}\text{C}$): (●) 120, (□) 140, (Δ) 160, (◊) 180.

It is of interest to observe in Figure 9 that over the range of temperatures investigated, namely from 80 to 130 $^{\circ}\text{C}$, the log G' versus log G'' plot for the 10:90 Kraton 1107/Flcoteac 95BHT mixture shows a single curve that is virtually independent of temperature, behavior typical of homogeneous polymer melts or solutions. We did not take measurements at temperatures below 80 $^{\circ}\text{C}$, since 80 $^{\circ}\text{C}$ was already very close to the glass transition temperature of the PS endblock in Kraton 1107. We speculate that in this mixture the Kraton 1107 formed a discrete phase in the form of micelles, which was then dispersed in Flcoteac 95BHT, the continuous phase, or was dissolved completely in the Flcoteac 95BHT, forming a continuous phase. It is worth mentioning that at room temperature the sample was brittle, which is char-

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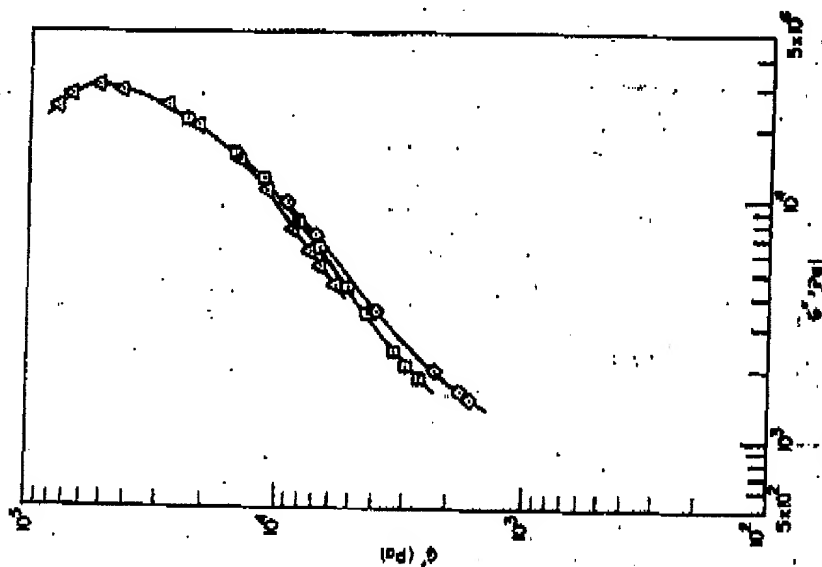


Fig. 10. Log G' versus log G'' for Kraton 1111 at various temperatures ($^{\circ}\text{C}$): (Δ) 200, (□) 240, (◇) 280.

Kraton 1111 has about 23 wt% of PS endblock, whereas Kraton 1107 has about 15 wt% of PS endblock (see Table I). It can, therefore, be concluded that the block length ratio of a block copolymer greatly influences its T_g , as predicted by Leibler's theory.¹¹

When Picozac 95BHT was added to Kraton 1111, to form a 70:30 mixture, apparently the T_g of the mixture was not reached even at 240 $^{\circ}\text{C}$, and thus log G' versus log G'' plots do not give a correlation that becomes independent of temperature, as may be seen in Figure 11. However, as the amount of Picozac 95BHT in the mixture was increased, we were able to determine the T_g of the 50:50 and 30:70 Kraton 1111/Picozac 95BHT mixtures, as summarized in Table III. It is seen in Table III that the addition of Picozac 95BHT has lowered the T_g of Kraton 1111, but values of T_g for the Kraton 1111/Picozac 95BHT mixtures are much higher than those for the Kraton 1107/Picozac 95BHT mixtures.

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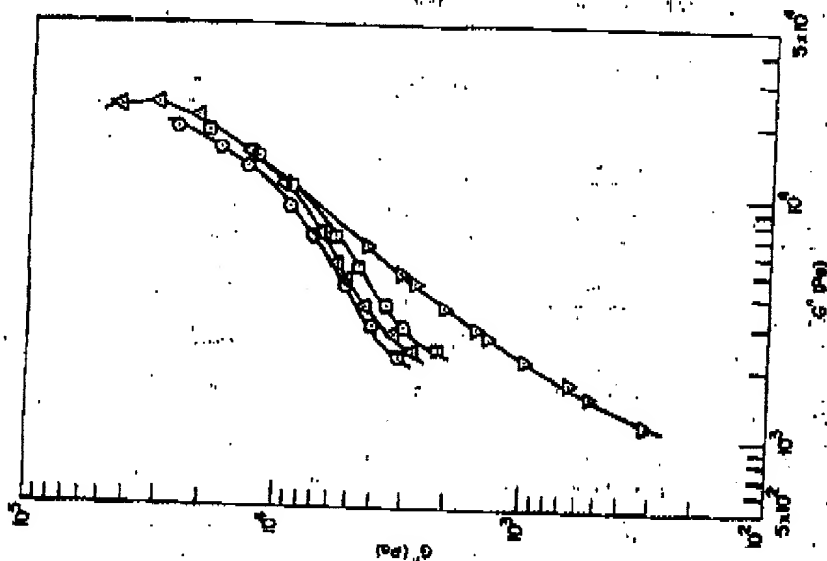


Fig. 11. Log G' versus log G'' for the 70:30 Kraton 1111/Picozac 95BHT mixtures at various temperatures ($^{\circ}\text{C}$): (○) 200, (Δ) 240, (□) 280, (◇) 320.

DISCUSSION

The Role of Picozac 95BHT in Mixtures with Kraton 1107 or Kraton 1111

It has been shown above that the addition of Picozac 95BHT to Kraton 1107 or Kraton 1111 has resulted in the following: (1) the plateau modulus decreased and the T_g of the PI endblock increased as the amount of Picozac 95BHT increased, and (2) the T_g decreased as the amount of Picozac 95BHT increased. According to the literature,⁸ Kraton 1107 that contains less than about 15 wt% of PS endblock has *spherical* microdomains of polystyrene. Galot⁸ reported that no morphological change could be observed when the concentration of a homopolymer was varied in either SI or SB diblock copolymer. Moreover, using electron microscopy Kraus and coworkers¹² in-

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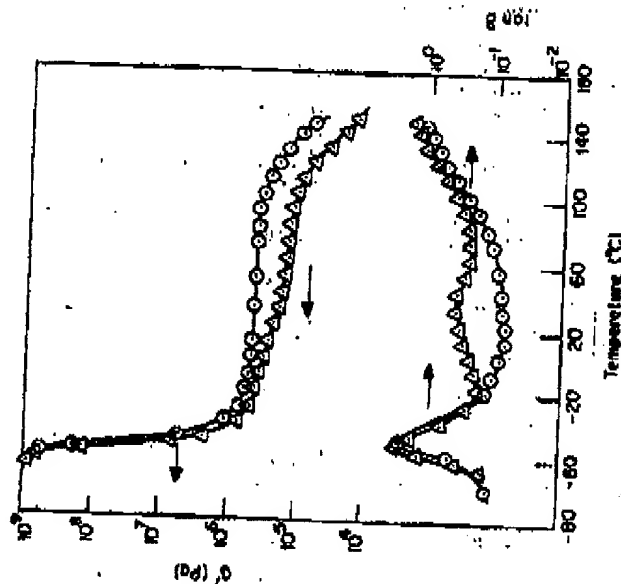


Fig. 12. Log G' and $\tan \delta$ versus temperature: (1) Kraton 1107, (2) Kraton 1107/PI homopolymer mixtures.

Kraton 1107 and Picozac 95BHT. The following observations are worth noting in Figure 13: (1) values of G' for Kraton 1111 remain almost unchanged with increasing ω , behavior typical of AB₄-type block copolymers; (2) values of G' for the 70:30 Kraton 1111/Picozac 95BHT mixtures show a very weak dependence on ω ; (3) values of G' for the 60:40 Kraton 1111/Picozac 95BHT mixtures increase moderately with increasing ω ; and (4) values of G' for the 30:70 Kraton 1111/Picozac 95BHT mixtures increase rapidly with increasing ω . Note furthermore that over the range of ω investigated, values of G' for the 70:30 and 60:40 Kraton 1111/Picozac 95BHT mixtures are lower than those of the Kraton 1111, but values of G' for the 30:70 Kraton 1111/Picozac 95BHT mixtures become larger than those of the Kraton 1111 at an ω of about 1 rad/s and greater. Similar observations can also be made for the mixtures of Kraton 1107 and Picozac 95BHT (see Fig. 14). On the other hand, when either an organic solvent or polyisoprene homopolymer is added to an SIS block copolymer, values of G' and G'' for the mixture will always be lower than those for the block copolymer over the entire range of ω , as long as the T_g of the mixture is far below room temperature.

Individual T_g suggested that 1.0 s be used as the time scale of the bonding process, which is equivalent to 1.0 rad/s in dynamic measurements, and that compressive creep compliance be 10^{-6} Pa⁻¹ or more, which is equivalent to a G' of 3×10^5 Pa or less, as by Kraus and Rehner¹¹ pointed out, for an adhesive to have a satisfactory tack property. According to this criterion, one

investigated the morphology of mixtures of a block copolymer and a tackifying resin [poly(α -pinene) or polyterpene] and reported that there was no change in the morphology before or after the tackifying resin was added to the block copolymer. Therefore, the addition of Picozac 95BHT to Kraton 1107 should not change the morphological state of the PS domains. In other words, Picozac 95BHT plays, in part, the role of a diluent in mixtures with Kraton 1107.

However, Picozac 95BHT does more than just dilute a block copolymer, whereas ordinary organic solvents have dilution effects only. It should be remembered that the T_g of Picozac 95BHT is 43°C. As discussed above in reference to Figures 2 and 3, Picozac 95BHT has not only decreased the plateau modulus of the block copolymer but has also increased the T_g of the PI midblock of the block copolymer. However, organic solvents could not have increased the T_g of the block copolymer, since the T_g 's of organic solvents are much lower than the T_g of the PI midblock of the block copolymer. As mentioned above, Picozac 95BHT is an aliphatic hydrocarbon containing cyclic structures. We believe that the cyclic structures present in Picozac 95BHT are responsible for such a high T_g (i.e., 43°C), which then contributes, in mixtures with an SIS block copolymer, to the observed increase in T_g . It is worth pointing out that when the C_{60} stream of petroleum hydrocarbons is polymerized only into straight chains without cyclization, the T_g of the resultant linear aliphatic hydrocarbons with $M_n = 1100$ cannot possibly have a $T_g = 43^\circ\text{C}$. For example, the T_g of a polyisoprene homopolymer with $M_n = 75,000$ is about -60°C . Therefore one would not expect to observe that the addition of polyisoprene homopolymer to an SIS block copolymer could affect its T_g . This indeed is borne out, as may be seen in Figure 12, which gives plots of G' and $\tan \delta$ versus temperature for the 70:30 Kraton 1107/PI homopolymer mixtures. It should be mentioned that the polyisoprene homopolymer used has $M_n = 75,000$, which is close to the molecular weight of the PI midblock in Kraton 1107, and it has a microstructure, which is identical with that in the rubbery midblock of Kraton 1107.

It is seen in Figure 12 that the addition of polyisoprene homopolymer to Kraton 1107 has lowered its G_n^0 but has not affected its T_g . The additional $\tan \delta$ peak, which appears between 0 and 30°C in Figure 12, is believed to be related to the entanglement slippage of the polyisoprene homopolymer molecules, which can move freely, whereas the movements of the block copolymer molecules are restricted, since they are physically crosslinked in this temperature range. The observed decrease in plateau modulus G_n^0 for the 70:30 Kraton 1107/PI homopolymer mixture results from the G_n^0 of the polyisoprene homopolymer, which is lower than the G_n^0 of the Kraton 1107. On the other hand, the observed decrease in plateau modulus G_n^0 (see Fig. 2) for the Kraton 1107/Picozac 95BHT mixtures (see Fig. 2) results from the dilution effect, i.e., the increased value of the molecular weight M_c between entanglement spacings in the mixture. It should be remembered that the plateau modulus G_n^0 of a polymer, with molecular weight M greater than M_n , is inversely proportional to M_c (see eq. (2)).

Figure 13 gives plots of G' and G'' versus angular frequency ω for Kraton 1111 and for mixtures of Kraton 1111 and Picozac 95BHT at room temperature. Similar plots are given in Figure 14 for Kraton 1107 and for mixtures of

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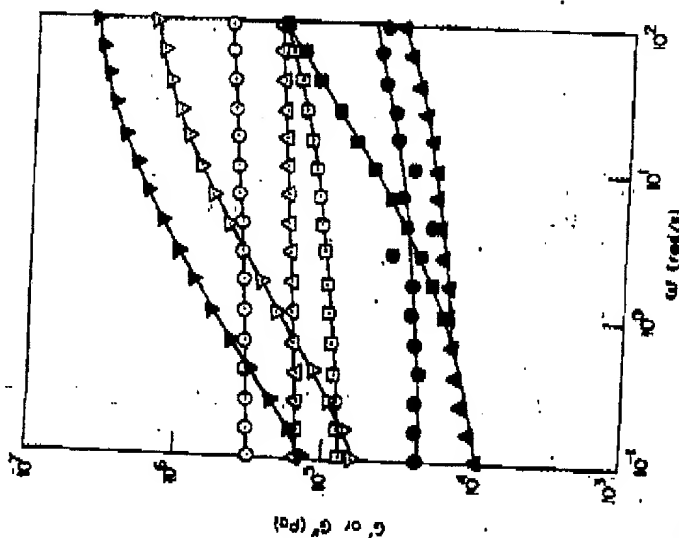


Fig. 14. Log G' and log G'' versus log ω at 25°C: (○, △) Kraton 1107/Picoteac 95BHT = 50:50; (□, ▽) Kraton 1107/Picoteac 95BHT = 30:70. Open symbols are for G' and closed symbols for G'' .

the PS endblock in the block copolymer. When Picoteac 95BHT with $T_g = 45^\circ\text{C}$ is added to Kraton 1107 and the temperature is raised slowly above the T_g of the PS domains (i.e., above 100°C), it is expected that Picoteac 95BHT will be softened and then either will act as a diluent if it is compatible (or soluble) with the block copolymer or will form a separate phase if it is incompatible (or insoluble) with the block copolymer. If Picoteac 95BHT is compatible with Kraton 1107, we would expect intuitively that it will associate more with the PI midblock than with the PS endblock of Kraton 1107, since the chemical structure of Picoteac 95BHT is much closer to the structure of polyisoprene than to that of polystyrene. If Picoteac 95BHT associates (i.e., is compatible) with the PI midblock of Kraton 1107, it will then act to dilute the concentration of the PS domains in the mixture, and thus the dissolution of PS domains with increasing temperature may be accelerated, yielding lower values of T_g as the amount of diluent is increased. This apparently is what has taken place (see also Table III).

The diffusion effect on T_g may best be observed when a polyisoprene homopolymer is added to an SIS block copolymer. Figure 15 gives log G' versus log G'' plots for the 50:50 Kraton 1107/PI homopolymer mixture at temperatures ranging from 120 to 210°C . The PI homopolymer used has a molecular weight of 75,000 and

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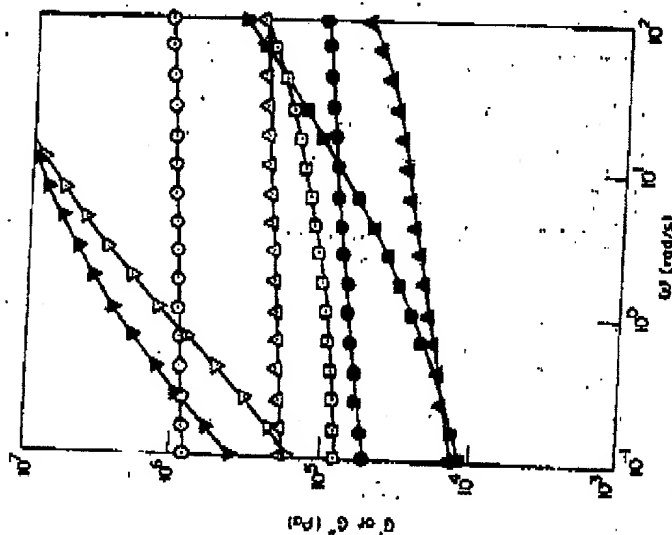


Fig. 13. Log G' and log G'' versus log ω at 25°C: (○, △) Kraton 1111/Picoteac 95BHT = 50:50; (□, ▽) Kraton 1111/Picoteac 95BHT = 30:70. Open symbols are for G' and closed symbols for G'' .

can be deduced from Figures 13 and 14 that the values of G' for the 30:70 Kraton 1111/Picoteac 95BHT mixture and also for the 30:70 Kraton 1107/Picoteac 95BHT are too high for these mixtures to be effective as pressure-sensitive adhesives.

From the point of view of the cohesive strength required during the debonding process, a high value of G'' is desired, since G'' reflects the ability to dissipate strain energy. Deblignat¹² suggested, also, that 0.01 s be used as the time scale of the debonding process in the probe tack test, which is equal to 100 rad/s in dynamic measurement. The values of G'' at 100 rad/s for the 50:50 Kraton 1111/Picoteac 95BHT mixture (also, for the 50:50 Kraton 1107/Picoteac 95BHT mixture) is even greater than that for Kraton 1111 (or Kraton 1107) itself. Therefore, when we consider that the debonding step occurs at 100 rad/s, values of G'' for the 50:50 Kraton 1111/Picoteac 95BHT and 50:50 Kraton 1107/Picoteac 95BHT mixtures are sufficiently high to offer satisfactory adhesive and cohesive strengths.

The Effect of Picoteac 95BHT on the Order-Disorder Transition Behavior of Kraton 1107 and Kraton 1111

Let us now consider the rheological behavior of the mixtures of Picoteac 95BHT with Kraton 1107 and Kraton 1111 at temperatures above the T_g of

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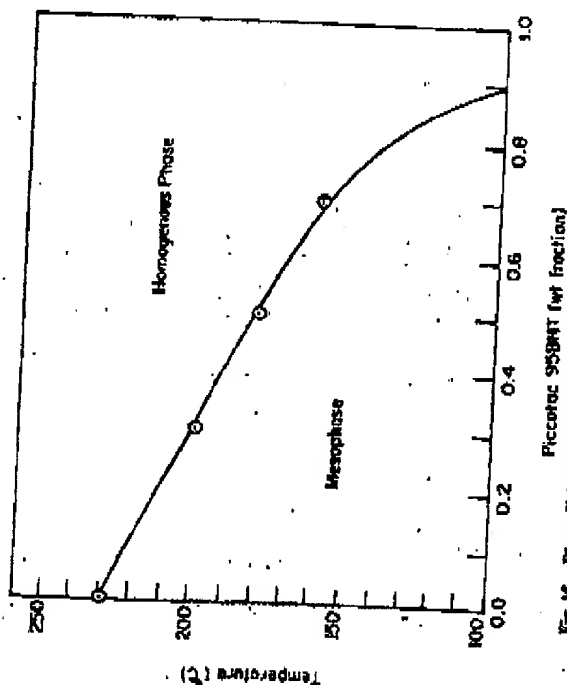


Fig. 16. Phase diagram for the Kraton 1107/Picoteac 95BHT mixtures.

Roe and coworkers²⁰ have also used the SAXS technique to investigate the order-disorder transition behavior of mixtures of a linear SB diblock copolymer and a polybutadiene homopolymer and reported that T_c decreased with increasing amount of polybutadiene homopolymer added. The conclusion drawn by these SAXS studies is in agreement with that drawn above, which utilized a rheological analysis, i.e., plots of $\log G'$ versus $\log G''$.

In the present study, we also investigated the phase equilibria for the Kraton 1107/Picoteac 95BHT mixtures using a light-scattering device. We found that there was no cloud point detectable for the mixtures in the range of temperatures from room temperature to about 250°C, over the entire range of blend compositions, indicating that no macrophase separation occurred for the Kraton 1107/Picoteac 95BHT mixtures. Therefore, we can conclude that the Kraton 1107/Picoteac 95BHT mixtures are truly compatible. This observation has allowed us to construct a phase diagram for the Kraton 1107/Picoteac 95BHT mixtures, as given in Figure 16, when combined with the values of T_c as determined from $\log G'$ versus $\log G''$ plots (see Table III). The solid curve in Figure 16 represents the boundary between the mesophase and homogeneous phase. It should be mentioned that the phase diagram given in Figure 16 is one of the many possible phase diagrams for mixtures of a block copolymer and a homopolymer, as recently developed by Whitmore and Noolandi.²¹

Whitmore and Noolandi²¹ constructed phase diagrams for mixtures of an SB diblock copolymer and a homopolymer, using a theory based on functional integral formalism, and predicted, for a symmetric copolymer with degree of polymerization Z_c and an asymmetric copolymer with degree of

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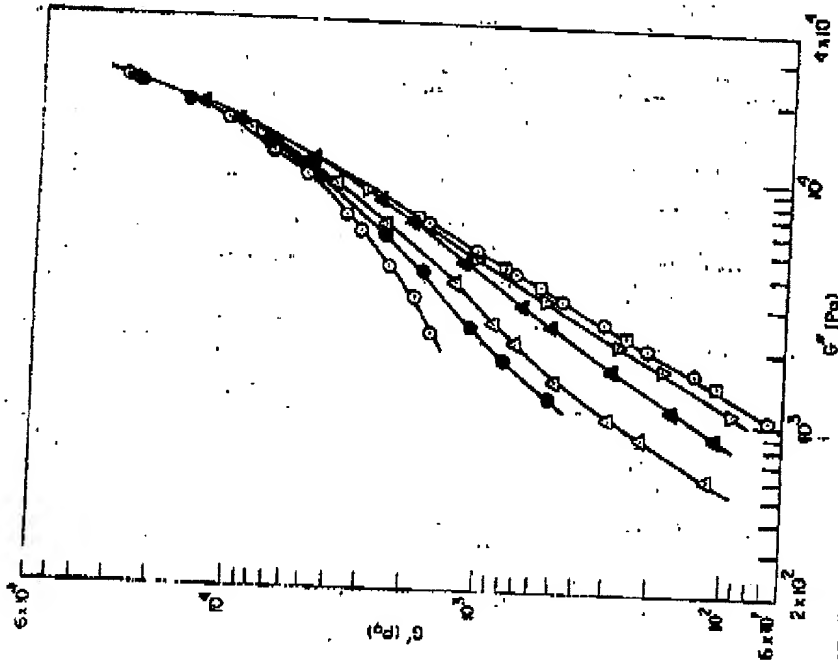


Fig. 15. $\log G'$ versus $\log G''$ for the 50:50 Kraton 1107/PI homopolymer mixtures at various temperatures (°C): (○) 120, (△) 140, (□) 150, (◇) 160, (○) 170, (△) 180, (□) 190, (◇) 200, (○) 210.

the block copolymer Kraton 1107. It is shown in Figure 15 that the values of G' become independent of temperature at about 200°C, which indicates that the mixture has become a homogeneous phase. In other words, the values of T_c for the 50:50 Kraton 1107/PI homopolymer mixtures is about 200°C, which is about 30°C lower than the T_c of the block copolymer itself (see Fig. 7 and Table III). Since there is no question about the compatibility between the polyisoprene homopolymer ($M_w = 75,000$) and the polyisoprene midblock ($M_w = 120,000$) in Kraton 1107, one can conclude from Figure 15 that the T_c of Kraton 1107 should decrease with the addition of the polyisoprene homopolymer.

Earlier, Kraus and Hashimoto²⁷ utilized the SAXS technique to investigate the order-disorder transition behavior of mixtures of a midblock-associating resin (polyterpene) with linear or radial SB diblock copolymer. They reported that the T_c of the block copolymer decreased in the presence of the midblock-associating resin, although they did not study the composition dependence.

when $Z_H > 0.25Z_C$, (2) T_g remains constant when $Z_H = 0.25Z_C$ and (3) T_g decreases when $Z_H < 0.25Z_C$. Our experimental results are in qualitative agreement with the theoretical predictions of Noolandi and coworkers.^{22,23} For the Kraton 1107/Picoteac 95BHT and Kraton 1111/Picoteac 95BHT mixtures, we note that $Z_H < 0.25Z_C$. However, a quantitative comparison between our experimental results and the theoretical predictions of Noolandi and Noolandi²² is not possible for the following reasons. (1) The theory is based on an A-B-type diblock copolymer, whereas the block copolymers used in our experiment are ABA-type triblock copolymers. (2) The theory assumes lamellar microstructures in the mesophase of the block copolymer, whereas, according to the literature,²⁴ the type of block copolymer investigated in our study most likely has spherical microstructures in the mesophase. It is interesting to observe, however, that these differences do not seem to affect much the general features of phase equilibrium diagrams.

CONCLUDING REMARKS

In the present investigation, we have shown that when a midblock-associating resin, specifically, Picoteac 95BHT, is mixed with an SIS triblock copolymer (namely, Kraton 1107 or Kraton 1111), the plateau modulus G_N^0 is lowered and the glass transition temperature T_g of the rubbery polyisoprene midblock is raised. These experimental results seem to indicate that Picoteac 95BHT is compatible (or miscible) with the polyisoprene phase in the SIS block copolymer. Compatibility of a low molecular weight resin with a block copolymer appears to be necessary for it to become an effective tackifying resin for pressure-sensitive adhesives. It has been shown in this study that the concentration of midblock-associating resin in a mixture with a block copolymer, the block-length ratio, and total molecular weight of block copolymer play vital roles in achieving the desired modulus and glass transition temperature needed for pressure-sensitive adhesives. In a future study we will investigate the effect of the chemical structures of midblock-associating resins on the viscoelastic behavior in mixtures with a block copolymer.

Using plots of $\log G'$ versus $\log G''$, we have determined the thermally induced order-disorder transition temperature T_i of mixtures of an SIS block copolymer and a midblock-associating resin. It has been observed that T_i decreases with increasing amounts of Picoteac 95BHT, which was also observed when a polyisoprene homopolymer was added to the same block copolymer. In view of the fact that the molecular weight of Picoteac 95BHT is very small compared with that of the polyisoprene midblock in the block copolymer, Kraton 1107 or Kraton 1111, the experimental result is consistent with the theoretical predictions of Noolandi and coworkers.^{22,23} The T_i determined from $\log G'$ versus $\log G''$ plots allowed us to construct a phase diagram for the mixtures investigated. In this regard, $\log G'$ versus $\log G''$ plots are considered to be very useful for investigating the thermally induced order-disorder transition behavior in mixtures of a block copolymer and a homopolymer.

In a future paper, we will report on the viscoelastic behavior and thermally induced order-disorder transition in mixtures of a block copolymer and an midblock-associating resin.

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Tack and Viscoelasticity of Block Copolymer Based Adhesives[†]

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Tackification of block copolymers of the linear ABA or radial (AB)_n type, in which the center block (B) is in the rubbery state at use temperature, follows principles established for other rubbery polymers except for peculiarities of the system introduced by the block copolymer structure. Successful pressure-sensitive adhesives result wherever the tackifier is compatible with the rubbery phase, which forms the continuum. Connectivity of the hard phase generally leads to loss in compliance, making tack ultimately contact-ture and contact pressure. A previously explored criterion for contact limitation, defining a critical minimum 1-second creep compliance, appears to be valid for block polymer-based adhesives, as is the rule that an effective tackifier must raise T_g (in the present case of the rubbery component) while also acting as a plasticizer.

Although viscoelastic processes play an exceedingly important role in the tack phenomenon, quantitative correlations for block polymer adhesives are difficult to establish. Nevertheless, some semi-quantitative relations have been developed. They are, in addition to the contact criterion, a correlation of tack and dynamic loss modulus and a criterion for tackifier compatibility with the rubbery phase.

INTRODUCTION

Anyone who has handled a piece of pressure-sensitive adhesive tape has an intuitive grasp of the phenomenon of "tack". Webster's dictionary defines it as "the quality or state of sticking or adhering; adhesiveness; stickiness". A little additional thought reveals it as a complex property, involving a bonding and a debonding process carried out in fairly rapid succession. In the bonding stage the objective is that maximum molecular contact be established between the soft adhesive and the microscopically rough substrate. Subsequent debonding is essentially an adhesion test, the outcome of

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situation one would like to increase segmental friction and hence the value of F . This can be done by using a soluble low molecular weight resin of substantially higher T_g than that of rubber, i.e., a tackifier. The tackifier does loosen up the entanglement network and so increases the compliance in the entanglement plateau and terminal regions, but it also raises T_g and so moves the use temperature of the adhesive composition closer to its transition region. These relationships are illustrated schematically in Figure 1. Note how at the use temperature the polymer does not satisfy Eq. (1), but the tackified composition does.

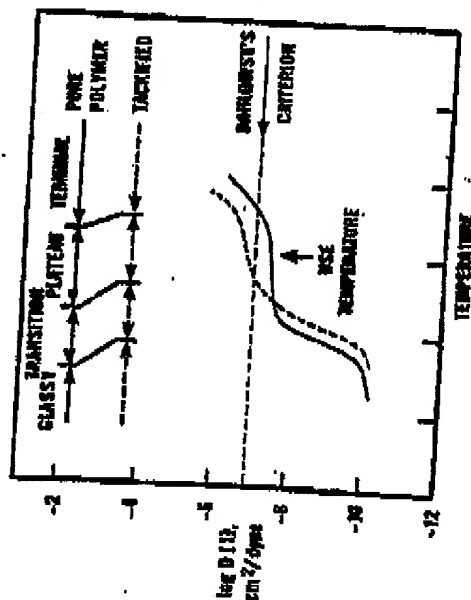


FIGURE 1 One second creep compliance vs. temperature of a high molecular weight amorphous polymer before (—) and after (---) incorporation of a tackifier.

The above analysis is also valid for block polymer-based adhesives, although some additional factors become important. The block polymers of principal interest here are the linear and radial tri- and multiblock polymers of butadiene or isoprene and styrene: SBS or SIS and (SB)_x or (SI)_x, where $x > 2$. These polymers are well known to undergo microphase separation forming domain structures. It has been shown that their outstanding advantage over homopolymers or random copolymers is holding power, derived from the persistence of the domain structure in the tackified adhesive compositions.⁷ The polystyrene domains act as multifunctional physical cross-links and filler particles and so greatly diminish shear creep at long times. The tackifier thus should be incompatible with the polystyrene domains, but compatible with the rubbery polydiene phase. Moreover, the latter should be the only continuous phase, since connectivity of the polystyrene domains greatly decreases the compliance in the temperature-time

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which will depend on the extent of contact established in the bonding stage, the strength of the intermolecular forces acting at the adhesive/substrate interface and the rheological properties of the adhesive layer. (In many cases a substrate may be considered to be infinitely rigid.)

A criterion for the establishment of contact on a microscopic scale was proposed several years ago by Dahlquist.⁴ It states that the compressive creep compliance on the time scale of the bonding process (ca. 1 sec) should be of the order of 10^{-7} cm²/dyne or larger, i.e.

$$D(t) \geq 10^{-7} \text{ cm}^2/\text{dyne.} \quad (1)$$

Since $D(t)$ is substantially smaller, serious loss in tack will result from relaxation of contact. Clearly, we have here the first crucial influence of a viscoelastic property of the adhesive on the tack phenomenon.

In the debonding step we are dealing with the adhesion of a soft viscoelastic material to a rigid surface. This basic problem has been studied extensively in the literature, most recently by Gent, Andrews and Kinloch.²⁻⁴ These authors employed the concept of a characteristic adhesive failure energy, θ , defined as the change in free energy of deformation with the area of a growing crack at the interface, to demonstrate the role of viscoelastic processes in the mechanics of adhesive failure. Specifically, Andrews and Kinloch³ were able to show that

$$\theta = \theta_0 F(\alpha_T) \quad (2)$$

where θ_0 is an "intrinsic failure energy" which, in absence of covalent bonding, is closely related to the thermodynamic work of adhesion. The function F represents the viscoelastic contribution by the adhesive, α being the crack propagation velocity and α_T the time-temperature shift function of linear viscoelasticity.⁵ Although tack is generally not measured in test geometries conducive to evaluation of θ and the resulting tack-values are not necessarily be simply related to θ , Eq. (2) can be used to gain useful insight into tack and tackification. Since F is a monotonically increasing function of α_T , a quantity which in turn increases strongly in moving from the rubbery region of viscoelastic response toward the transition region, it is possible to attain reasonable values of θ even when θ_0 is small, i.e. with polar adhesives relying entirely on dispersion forces for bonding to the substrate. Equation (2), of course, also makes clear that the chemical nature of the substrate and its interaction with the adhesive will have an effect on adhesion and tack.

High molecular weight rubbers, block polymers included, have little or no increase first of all the contact criterion (Eq. 1) is not satisfied. It can, of course, be met by the addition of a plasticizer or low molecular weight tackifiers function in two ways. They loosen up the entanglement network and usually decrease segmental friction. However, in the present

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region of interest, resulting in failure to meet the contact criterion. Fortunately, the use of large quantities of polydiene-compatible tackifiers tends to prevent polystyrene domain connectivity, such as results from cylindrical or lamellar morphologies. Still, formulation of adhesives of highest tack becomes difficult with block polymers containing more than 30% styrene.⁷

The present work is a continuation of earlier studies from this laboratory on tackification of diene-styrene block polymers.^{7,8} It examines some of the relationships developed in more detail and addresses itself to some previously uninvestigated questions.

EXPERIMENTAL

Materials

The block polymers used were commercial radial-structure block copolymers manufactured by Phillips Petroleum Company (Table I).

TABLE I
Polymer characteristics^a

Polymer	Composition	$M_w/1000$	$M_0/1000$
Solprene®418	85 :15 isoprene/styrene	300	220
Solprene®417	80 :20 butadiene/styrene	190	150
Solprene®416	70 :30 butadiene/styrene	140	110
Solprene®414	60 :40 butadiene/styrene	130	100

^a Nominal properties.

[†] A trademark of Phillips Petroleum Company.

Tackifying resins were likewise of commercial manufacture. Their chemical type and origin are listed in Table II.

TABLE II

Resin	Type	Source
Foral 85	Resin ester	Hercules, Inc.
Winglack 95	Polycyclopentadiene	Goodyear Chemical Co.
Super Sio-Tac 80	Polysulfone	Richfield Chemical Co.
Zonarez 7085	Polyisobutylene	Arizona Chemical Co.
Zonarez B-95	Poly(2-vinylpyridine)	Arizona Chemical Co.
Pico Alpha 415	Poly(styrene)	Hercules, Inc.
Kristalex 1120	Poly(2-methylstyrene)	Hercules, Inc.

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Adhesive formulations and testing

A simple basic formulation was used throughout this study:

Polymer	100
Tackifier	as specified
Stabilizer†	1

Variable tackifier concentration series were prepared with Solprene 418 using Foral 85 and Winglack 95, respectively. In addition the various resins were evaluated at 100 phr concentration in both Solprene 418 and 417. Solprene 416 and 414 were used with 100 phr Foral 85 only.

Formulations were mixed 30 minutes at 50 rpm in a Brabender Plasticorder under a nitrogen blanket. The mixing chamber was heated with oil circulated from a bath maintained at 180°C.

The pressure-sensitive films for the tack measurements were prepared by a hot melt molding procedure. Small portions of the mix were pressed between Teflon-coated foil and 2-mil Mylar backing with platens at 150°C to form films. Slit stock was used to control the film thickness at 0.06 ± 0.01 mm. The probe tack values of these films were determined one day after preparation.

Tack measurements were made exclusively with a Polyken Probe Tack Tester, Testing Machines, Inc., Amityville, N.Y.; test results reported are averages taken from five specimens. Contact time was 1 second, contact pressure 100 grams/cm², and separation rate 1 cm/second. Unless otherwise stated the test temperature was $25 \pm 1^\circ\text{C}$ with a polished stainless steel probe.

Probe tack determinations at temperatures above 25°C were obtained by enclosing the probe, specimen, and specimen carrier in a heated chamber. Specimens were placed in the heated chamber 20-30 minutes before testing.

Viscoelastic measurements

Dynamic viscoelastic measurements were carried out in shear, using a Rheovibron Model DDV-II Viscoelastometer (Toyo Instruments Co., Japan). The test specimen was a 3 mm square of 0.4-0.5 mm thickness sandwiched between brass plates. Creep measurements were carried out at 22°C in tension on $0.16 \times 0.685 \times 4$ cm strips. A constant applied stress of 3.3×10^5 dynes/cm² was used in all creep determinations. The creep of the adhesive formulations was not strictly linear. However, non-linearity was modest; typically, a 2.5-fold increase in stress caused a 20% increase in the measured compliance. A correction was applied for diminishing cross-section during the creep experiment. Details of this calculation are to be published elsewhere.

† Ingonox 8018.

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RESULTS AND DISCUSSION

creep compliance

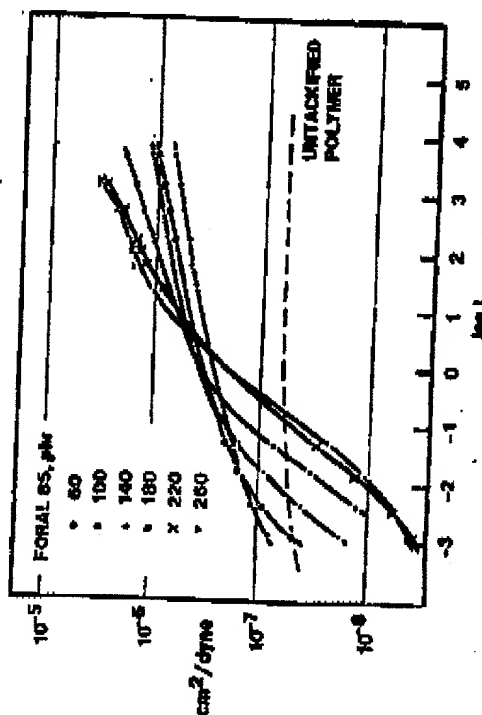
Using the Deblquis' contact criterion requires knowledge of the 1-second creep compliance (Eq. 1). Unfortunately, $D(t)$ is not easily measured directly, time being too short after the (hypothetically) instantaneous application of stress. Creep compliances can be calculated from dynamic measurements, these are usually performed at higher frequencies and so furnish values $D(\omega)$ at shorter times only. In the present study both types of measurements are combined to obtain $D(t)$ by interpolation. For times longer than 10 seconds creep was measured directly (in tension) and values of $D(\omega)$ at times shorter than 0.1 sec. were calculated from dynamic shear data by the approximation method of Riancho and Markovitz.⁹

$$J(t) \approx \{J'(\omega)^2 + [J''(\omega)]^2\}^{1/2}, t = \omega^{-1} \quad (3)$$

the well known relation

$$3D(t) = J(t) \quad (4)$$

is applicable to incompressible materials—a good assumption for soft rubbery samples. Here ω is the angular frequency in radians/sec, J' and J'' are the dynamic storage and loss compliances in shear and $J(t)$ the shear creep compliance.



RE 2 Creep compliance at 22°C for isoprene-styrene block polymer (Solprene 418) with level of resin ester tackifier.

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Figure 2 shows $D(t)$ at 22°C for a series of adhesives formulated from Solprene 418 and Foral 83 tackifier, the level of the latter increasing from 60 to 260 phr in 40 phr increments. The response of the untackified block polymer is seen to be extremely flat. This reflects the highly elastic character of the block polymer resulting from the low T_g of its polyisoprene matrix and effective cross-linking by its polystyrene domains. Addition of tackifier increases the creep compliance at long times, the effect of a low molecular weight diluent. At very short times, however, $D(t)$ is decreased, because the zone toward longer times so that the more highly tackified compositions are now well inside the transition region from glassy to rubbery behavior.

At intermediate times there are multiple cross-overs. With the exception of the pure polymer, which has little tack, $D(t)$ lies comfortably above satisfactory tack. Table III shows that all six adhesive compositions have modulus at a fixed frequency of 35 Hz, illustrating the shift of the glass transition temperature of the rubbery phase, and the dynamic moduli at room temperature.

TABLE III

Effect of tackifier level on probe tack of Solprene 418 based adhesives

Tackifier	Level (phr)	T_g^{calc} (°C)	$G' \times 10^{-7}$ (dynes/cm²)	$G'' \times 10^{-7}$ (dynes/cm²)	$D(t) \times 10^7$ (cm²/dyne)	Probe tack (grams)
Foral 83	60	-22	0.27	0.095	2.7	1060
	100	-12	0.28	0.29	3.5	1610
	140	-4	0.48	0.94	3.9	1360
	180	14	1.80	2.55	3.8	1560
	220	24	2.55	2.65	1.8	1360
Winglack 95	260	33	4.60	1.75	1.8	1690
	60	-26	0.26	0.064	3.1	740
	100	-3	0.28	0.23	4.4	1170
	140	12	0.95	1.09	3.5	1440
	180	24	2.30	2.40	2.2	650

Similar data for Solprene 418/Winglack reveal the same general trends, except that tack exhibits a sharper maximum with resin concentration. Creep curves for these compositions are shown in Figure 3.

Figure 4 shows the creep behavior of Solprene 418 with five effective tackifiers at constant concentration (100 phr). The curves show remarkable

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TABLE IV

Comparison of tackifiers in Solprene-418 (100 phr)

Tackifier	$T(G_{max})$ (°C)	$G' \times 10^{-7}$ (dynes/cm ²)	$G' \times 10^{-7}$ (dynes/cm ²)	$D(1) \times 10^7$ (cm ² /dyne)	Probe tack (grams)
Wingback 95	-3	0.28	0.23	4.4	1170
Super Sta-Tac 80	-14	0.23	0.135	3.0	1090
Focal 85	-12	0.28	0.24	3.5	1010
Zonarez 7085	-2	0.34	0.34	3.4	1520
Pico Alpha 115	-10	0.38	0.46	3.6	1540
Zonarez B-85	-2	0.38	0.35	3.3	1120
Kristalex 1128	-4	0.80	1.70	<0.1	0

* Less than -40°.

Contact criterion†

In Ref. 7 a contact criterion, more conservative than the one of Dahlquist, was formulated in terms of the storage modulus at 35 Hz:

$$G'(35 \text{ Hz}) < 4 \times 10^6 \text{ dynes/cm}^2 \quad (5)$$

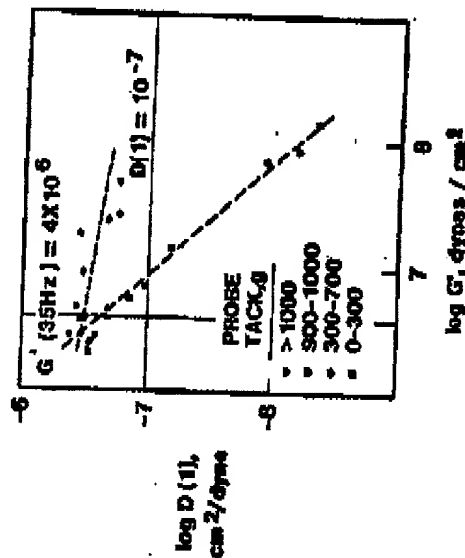


FIGURE 5 Comparison of contact criteria.

† Contact criteria are, of course, dependent on contact pressure, dwell time and surface roughness. The criteria discussed here are for the experimental conditions of the present study.

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similarly and all compositions again satisfy the Dahlquist criterion. Tack values are shown in Table IV, together with data for poly (o-methylstyrene) resin which is not a tackifier and which clearly does not meet the $D(1) > 10^{-7}$ criterion.

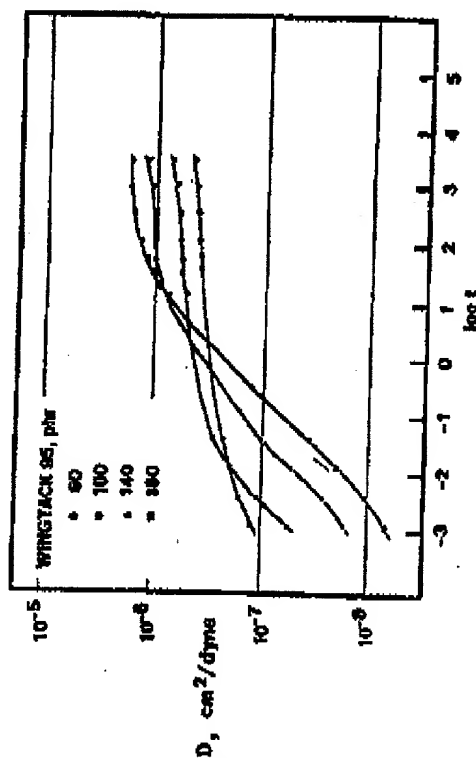


FIGURE 3 Creep compliance at 22°C for isoprene-styrene block polymer (Solprene-418) at varying level of polyisoprene tackifier.

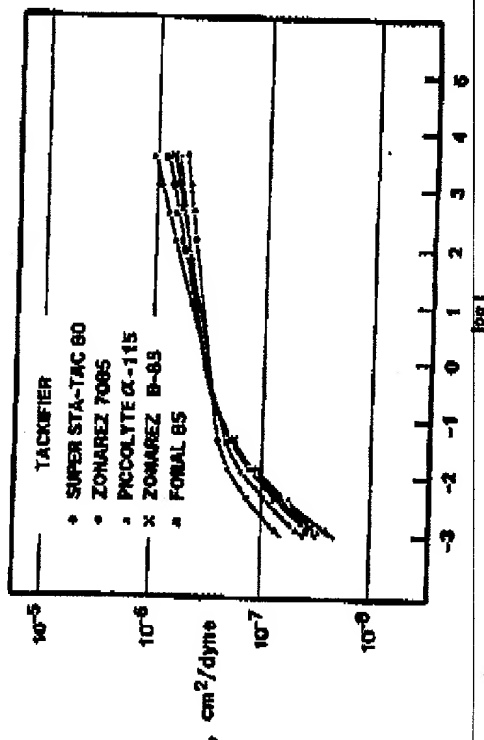


FIGURE 4 Creep compliance at 22°C for isoprene-styrene block polymer (Solprene-418) with 180 parts of various resins.

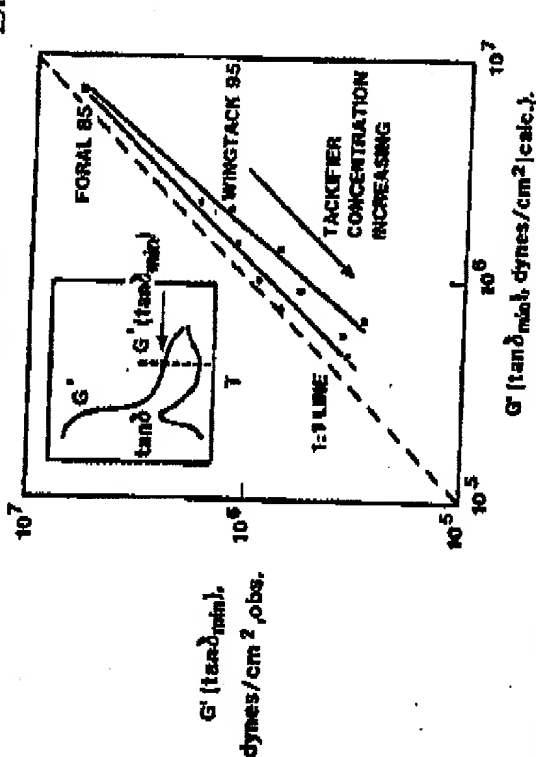


FIGURE 6 Observed vs. calculated storage moduli (35 Hz) at temperature of minimum in loss tangent. Data for Solprene 418.

The two tackifier concentration series (Table II) permit closer examination of the problem. As seen from Figure 6, the difference between observed and calculated $G'(\tan \delta_{\max})$ indeed increases with concentration, suggesting a stronger dependence than v_2^2 . However, it is obvious that the two tackifiers do not follow exactly the same concentration law. The best-fit exponents are 2.28 and 2.62, respectively, and their use would force very good agreement between calculation and experiment. However, this does not appear to be a particularly useful exercise. Instead, we note that Eq. (6) is independent of the nature of the diluent; it only considers loosening of the entanglement network and the reinforcing effect of the polystyrene domains. Moderate specific effects would, of course, be entirely conceivable. On the other hand, the substantial increases in T_g of the rubbery phase, caused by large amounts of tackifiers, shift the minimum in $\tan \delta$ into the region approaching the polystyrene domain glass transition. Some softening of polystyrene domains is, therefore, possible; Eq. (6) treats them as perfectly rigid. The fact that Wingtack 95 raises the position of the minimum in $\tan \delta$ more than Foral 85 would be consistent with this interpretation (Figure 7). Interestingly, the position of the $\tan \delta$ -maximum, accompanying the glass transition of the rubbery phase, is the same for the two tackifiers when the comparison is made at equal volume fraction. In spite of all this the degree of success of Eq. (6) in predicting $G'(\tan \delta_{\max})$ for a series of highly complex materials without the use of any adjustable parameters is quite satisfactory.

Figure 5 shows a mapping of $D(t)$ and G' (35 Hz). The data are taken from Tables III and IV and similar tests on butadiene-styrene block polymers (see Experimental). In the upper left quadrant both criteria are met and the probe tack value exceeds 700 g in all cases (all squares and circles). The Dahlquist criterion is seen to be remarkably good, with only minor violations near the critical compliance of 10^{-7} cm²/dyne.

The data of Figure 5 appear to group themselves along two lines. The points clustering about the dashed line are all for 100 phr of tackifier, with polymer and tackifier varying, while those along the dotted line represent variable tackifier levels. These are not fundamental correlations. They merely reflect the fact that for the two variable tackifier concentration series the compliance curves lie close together at $t = 1$, while the short-time compliances and the dynamic moduli (at $\omega = 1/s$) vary appreciably with concentration (Figures 2 and 3). For the adhesives at constant tackifier level the shapes of the creep curves are more nearly similar, hence the compliances vary inversely to the moduli.

Criterion for tackifier effectiveness in Diene-Styrene Block Polymers

Aras and Rollmann⁸ have shown that the value of the dynamic storage modulus of block polymer-based adhesives of the present type at the minimum in $\tan \delta$, located between the polydiene and polystyrene domain glass transitions (see inset of Figure 6), is approximately given by

$$G'(\tan \delta_{\min}) = v_2^2(\rho/M_e)RT(1 + 2.5c + 14.1c^2) \quad (6)$$

if the tackifier is soluble in the rubbery continuum, but not in the polystyrene domains which are assumed spherical. Here v_2 is the volume fraction of polymer in the polydiene phase, c the volume fraction of polystyrene domains in the entire composition, M_e the polydiene entanglement spacing in undiluted polymer, ρ the density, R the gas constant and T absolute temperature. If a prospective tackifying resin is compatible with and "alloys" with the polystyrene domains v_2 will remain unity, c will be increased by the tackifier and, very likely, some connectivity of the glassy phase will develop if the level of tackifier is high enough. Hence G' will greatly exceed the value calculated by Eq. (6). The same will be true if the resin is compatible with neither block and forms a third phase. In neither case will tack of the composition be enhanced. In this manner Eq. (6) becomes a criterion of suitability of a resin as a tackifier, to which must be added the condition that v_2 must increase T_g .

Using the adhesives used to demonstrate the validity of Eq. (6) were of the compositions of the present paper. It was observed that the equation holds almost quantitatively for pure block polymers ($v_2 = 1$), but for the v_2 concentration dependence appears to overestimate the modulus.

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100-200 g irrespective of contact time. To further illustrate these effects experiments were made in which the temperatures of the bonding and debonding steps were varied independently (Table VI). It is clear that adhesive C, while exhibiting very little tack at 25°C, gives excellent adhesion if the bonding temperature is sufficiently high.

TABLE V

Effects of dwell time and temperature on tack

	A Solprene-417 -Foral 85 ^a	B Solprene-416 -Foral 85 ^a	C Solprene-414 -Foral 85 ^a
200×10^7 cm ² /dyne, 25°C	2.2	0.7	0.12
$10^7 \times 10^7$ dynes/cm ² , 25°C, 35 Hz	0.45	1.38	6.9
$10^7 \times 10^7$ dynes/cm ² , 25°C, 35 Hz	0.18	0.79	1.8
Probe Tack, g			
25°, 1 sec. dwell	960	1120	70
50°, 5 sec. dwell	980	1250	170
50°, 1 sec. dwell	790	640	430
50°, 5 sec. dwell	840	690	760

^a 100 phr.

TABLE VI

Effect of bonding and debonding temperatures^a

Bonding Temp. (°C)	Time (sec.)	Debonding Temp. (°C)	Probe Adhesion or Tack (grams)
25	1	25	70
50	1	30	430
50	10	25	700
100	1	100	190
100	10	25	1440

^a Adhesive C of Table V, debonding rate 1 cm/sec.^b Time to cool to 25°C.

Figure 8 combines the points of the ascending branch of Figure 17 of reference 7 with the data of the present study on all adhesives satisfying the Dahlquist contact criterion. The result is a satisfactory, if somewhat scattered,

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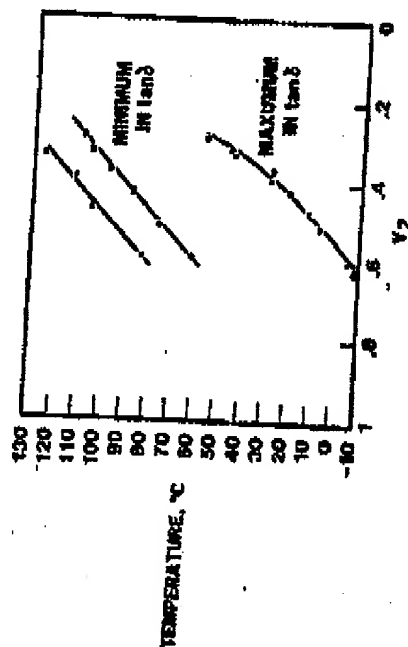


FIGURE 7. Positions of maxima and minima in loss tangent (35 Hz). Solprene 418 with Foral 85 (Δ) and Wingtack 95 (●).

The probe tack value

To explain different values in the probe tack test with various block polymer-based adhesives Kraus *et al.*⁷ attempted a correlation with the loss modulus at 35 Hz. It has been estimated^{1,10} that the time scale of the debonding step in the probe tack test is of the order of 0.01 sec which is roughly comparable to a dynamic test at 35 Hz, as $t = 1/\omega = 1/2\pi(35) = 0.005$ sec. Moreover, the loss modulus was chosen since it is proportional to energy dissipation and energy losses around the tip of growing cracks are well known to figure prominently in both cohesive and adhesive failure phenomena.^{2,3}

The result of this attempt was a curve with a maximum in tack at a loss modulus near 10^6 dynes/cm². The declining portion of the curve was ascribed to increasing degrees of contact limitation, as the storage modulus increases concurrently to values well above the contact criterion of Eq. (5). However, as shown above this criterion is rather conservative and contact limitation was not actually proven in the earlier study. To provide such proof one may be made of the fact that the tack of a contact-limited adhesive should respond to increasing dwell time and contact temperature. Table V shows an example.

Of the three adhesives, C fails both contact criteria (Figs. 1 and 5). A passes and B appears marginal. Only C responds significantly to increasing dwell time and temperature. For the others the tack value decreases with temperature, as expected. Indeed at 100°C all three adhesives gave tack values of

[†] Frequencies available on the Rheovibron apparatus are 3.5, 11, 35 and 110 Hz. An error of 10% in the frequency would not affect the results significantly.

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correlation. The only serious violation occurs for the Solprene 418/Wingtack 95 adhesive containing 180 phr of tackifier (see Table IV). The correlation is, of course, limited on the side of large values of G'' . Because these are rubbery adhesives, whose $\tan \delta$ will generally not exceed unity, G'' cannot increase indefinitely without also increasing G' , leading to eventual contact limitation of tack. In any case, the maximum probe tack possible with these adhesives appears to be in the vicinity of 1400 g.

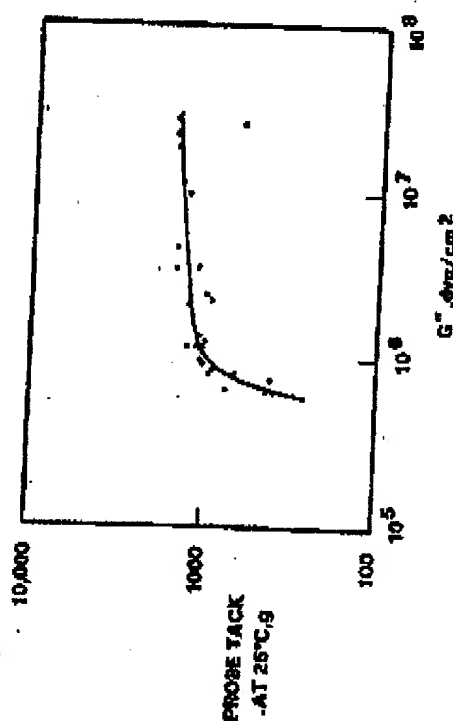


FIGURE 9 Tack vs. 35 Hz loss modulus.

The correlation of Figure 8 does not consider the possibility of an effect on tack of the magnitude of the intermolecular forces acting at the interface. Since the chemical composition of the adhesives varies appreciably (the data cover butadiene/styrene and isoprene/styrene block polymers of different styrene contents with different tackifying resins at several concentrations) some of the scatter could easily be due to this variable. In fact, the success of the correlation suggests that these interactions are roughly constant. Since the adhesives are essentially non-polar substances, the interaction with the (stainless steel) substrate is likely to be entirely by dispersion forces, which do not vary strongly among different hydrocarbon materials. That there is a significant contribution to tack from surface interactions is easily demonstrated by changing the probe material.

Tack vs. probe material

Table VII shows tack values for Solprene 418/Foral 85 (100 phr) adhesive against six different probe materials. The tack of this adhesive under the present conditions is not contact-limited. With only minor, probably in-

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significant, inversion at 50°C, tack decreases in the same order for the different materials at all temperatures. The fact that the organic polymers, but also aluminium, show increasing tack with rising temperature is not clearly understood. For the polymers one might visualize some (very limited) mixing at the interface, but this could hardly apply to aluminium.

TABLE VII

Tack as function of substrate material

Probe material	Probe Tack, g		
	25°C	35°C	50°C
Stainless steel	1280	1080	520
Glass	1040	960	360
Aluminium	410	598	600
Polypentenylene sulfide	280	360	630
Polyamide	170	150	270
Polytetrafluoroethylene	40	30	90

CONCLUSIONS

The results of this and earlier studies^{7,8} illustrate clearly the close connection between tack and viscoelasticity for block-polymer based pressure-sensitive adhesives. The correlations found seem valid, but they are essentially semi-quantitative and limited to certain aspects of the problem. A general theory of tack and adhesion seems a long way off, particularly for such complicated materials as block polymers. Foreseeable impediments are thermorheological complexity (multiphase block polymers do not follow simple time-temperature superposition), complications arising from non-linearity, and the detailed effects of the morphology on mechanical behavior. Added to this is, of course, the difficulty of the stress analysis problems involving complicated test geometries.

Of the three relationships between tack and viscoelastic properties discussed here, the Dahlquist contact criterion seems generally applicable to all pressure-sensitive adhesives. The correlation between tack and loss modulus has been demonstrated only for block polymers; it may or may not be of broader validity. The tackifier selection criterion has been tested with isolated compositions based on polyisoprene and polybutadiene homopolymers ($c = 0$ in Eq. 6) and found to apply.⁸ The utility of all these correlations lies, of course, mainly in the insight they provide into the mechanism of tack. In practice, it is always easier to measure the tack of a composition directly.

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Viscoelastic Behavior, Thermodynamic Compatibility, and Phase Equilibria in Block Copolymer-Based Pressure-Sensitive Adhesives

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The viscoelastic behavior, thermodynamic compatibility, and phase equilibria in block copolymer-based pressure-sensitive adhesives were investigated. The block copolymers investigated were: (1) polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) copolymer (KRATON® D-1102, Shell Development Company) and (2) polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) copolymer (KRATON® D-1107, Shell Development Company). The tackifying resins investigated were: (1) WINGTACK® 86 (Goodyear Tire & Rubber Company) and (2) PICCOTAC® 95BHT (Hercules Inc.). Samples of various compositions were prepared by a solution-casting method with toluene as solvent. Measurements of dynamic storage modulus (G'), dynamic loss modulus (G''), and loss tangent ($\tan \delta$) were taken, using a Rheometrics Mechanical Spectrometer. It was found that: (1) both WINGTACK 86 and PICCOTAC 95BHT were equally effective in decreasing the plateau modulus (G_p), and increasing the glass transition temperature (T_g) of the polyisoprene midblock of KRATON 1107; and (2) WINGTACK 86 was very effective in decreasing the G_p and increasing the T_g of the polybutadiene midblock of KRATON 1102, whereas PICCOTAC 95BHT was not. The observed difference between WINGTACK 86 and PICCOTAC 95BHT in decreasing the G_p and increasing the T_g of the polybutadiene midblock of KRATON 1102 (perhaps to SBS block copolymers in general) is explained by the values of the interaction parameter for WINGTACK 86 and KRATON 1102, and for PICCOTAC 95BHT and KRATON 1102. The interaction parameter was determined, using the piezoelectric quartz sorption method. Phase diagrams were constructed for the four block copolymer/tackifying resin systems investigated, using information obtained from both dynamic viscoelastic measurements and optical microscopy. It was found that when mixed with KRATON 1102, PICCOTAC 95BHT formed separate domains whereas WINGTACK 86 did not over the range of concentrations and temperatures investigated. This confirms the evidence obtained from two other independent experimental techniques, namely, dynamic viscoelastic measurements and the piezoelectric sorption method. We have concluded from the present study that PICCOTAC 95BHT is not as an effective tackifying resin as WINGTACK 86, when each is mixed with KRATON 1102. It is pointed out further that information on the order-disorder transition temperature T_o , which was determined from a rheological technique proposed by us, is valuable in determining optimal processing conditions for block copolymer-based pressure-sensitive adhesives.

KEY WORDS Block copolymer; dynamic viscoelastic properties; phase diagram; pressure-sensitive adhesives; tackifying resins; thermodynamic compatibility.

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INTRODUCTION

The adhesive industry in the United States is probably the largest and most complex market for formulated specialty polymers. Its steady increase is expected to continue in the years to come. Among the various kinds of adhesives, the demand for pressure-sensitive and hot-melt adhesives has grown significantly. Various types of elastomers are used in this branch of the industry. Although natural rubber still has the largest volume, adhesives based on synthetic elastomers have grown very fast in recent years. The block copolymers are gaining wide acceptance, due to their excellent balance of tack, adhesion strength and shear holding characteristics. The most widely used block copolymer in pressure-sensitive adhesives has a polystyrene block on both ends of a polydiene midblock (e.g., the ABA-type triblock copolymers). The usefulness of these block copolymers as adhesives is a direct consequence of their unique structure. The polystyrene endblock, which is incompatible with the polydiene midblock, separates on a microscopic scale to form polystyrene microdomains, thereby creating a physically-crosslinked network structure.^{1,2}

Since the elastomer alone is not sufficient to give rise to the desired levels of adhesion and tack, one usually adds low molecular weight hydrocarbons (e.g., aliphatic or aromatic hydrocarbons, polyterpenes, rosin and its derivatives), in order to improve its ability to wet the surface sufficiently and to form a bond of measurable strength upon contact. This low molecular-weight material is referred to as a "tackifying resin." Tackifying resins come in a variety of chemical structures and physical properties.³ They are thermoplastics and usually form an amorphous glass at room temperature.

Choosing the proper elastomer and tackifying resin pair is one of the most important tasks in obtaining successful adhesives which meet the required performance level, as determined by tack and the resistance to peel and shear. Tack is essentially a measure of viscous flow under conditions of high strain rates and low stress levels, while shear adhesion is a measure of viscous flow at low strain rates and intermediate stress levels. Peel adhesion may be considered to be a measure of the resistance to viscous flow at intermediate strain rates and high stress levels, as well as a measure of the cohesive strength of pressure-sensitive adhesives. It is certain that in a given adhesive system these properties tend to be mutually exclusive, so that a balance must be maintained on the desired performance requirements. Hence, the determination of an optimum concentration of tackifying resin, for instance, can be one of the most important tasks in producing successful adhesives. The higher the resin concentration, the greater the peel adhesion and surface tack, but the lower the cohesive strength will be.

Several factors must be considered when formulating an adhesive. Firstly, the tackifying resin and elastomer must be compatible. Unless the resin is compatible with the elastomer, the resin will form a dispersed phase and thus will not be able to reduce the modulus of the elastomer/resin blend, making the blend undesirable as a pressure-sensitive adhesive.⁴ When using an ABA-type block copolymer, a distinction must be made between the effect of midblock-associating

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resins and that of endblock-associating resins, for the following reasons. Aliphatic olefin-derived resins, rosin esters, polyterpenes, and terpene phenolic resins tend to associate with the polydiene midblocks and not with the polystyrene endblocks. The primary function of a midblock-associating resin is to develop tack in the thermoplastic elastomer. On the other hand, polyaromatics and the resins derived from coal tar or petroleum tend to associate with the polystyrene endblocks and not with the polydiene midblocks.

Secondly, information on the viscoelastic behavior of an adhesive is needed to evaluate its performance. The principal problem involved in the application of adhesives to substrates is rheological in nature. In order to have good tack, the viscosity of the elastomer/resin mixture must be lower than that of the elastomer itself, such that it can flow easily and is able to wet the surface sufficiently upon application. On the other hand, viscoelasticity information is required for understanding the ultimate properties of an adhesive. Since tack, shear adhesion, and peel strength are determined at different strain rates or stresses, viscoelasticity information (such as viscosity and elasticity, yield stress of the adhesive, and their dependencies on strain rate) must be well understood.

The testing of pressure-sensitive adhesives involves both bonding and debonding steps. For satisfactory performance in the bonding step, the material must be in a permanently deformable state, implying that it must possess the features typical of a liquid. However, satisfactory performance in the debonding step demands that the adhesive yield little under stress, and therefore behave essentially as a solid. A good adhesive adequately wets the substrate during its application, so that subsequent failure, when it occurs, is of a cohesive nature rather than an adhesive one. Thus, the viscoelastic behavior of adhesives is an important factor in performance evaluation. Therefore, it can be surmised that a better understanding of the significance of the type and concentration of tackifying resin on the viscoelastic behavior of pressure-sensitive and hot-melt adhesives is needed so as to provide better control of (or to improve) their end-use performance.

Very recently, we have conducted an investigation on the viscoelastic behavior, thermodynamic compatibility, and phase equilibria in block copolymer-based pressure-sensitive adhesives that were prepared in our laboratory. In this paper we will report the highlights of our investigation.

BACKGROUND

We will review very briefly some of the previous studies, which are directly related to the results of this study.

Viscoelastic behavior of mixtures of a block copolymer and a tackifying resin

Kraus and coworkers⁶⁻⁷ reported a series of experimental studies on the dynamic viscoelastic properties of mixtures of a block copolymer and a tackifying resin.

They reported that the use of a tackifying resin increased the glass transition temperature (T_g) of the polydiene midblock and decreased the dynamic storage modulus (G') in the plateau region, hereafter referred to as the plateau modulus (G_N^0). They stated that such characteristics are highly desirable for a low molecular-weight resin to be effective as a tackifying resin.

According to the classical concept of molecular viscoelasticity theory,⁸ G_N^0 for dilute polymer solutions is proportional to the square of the volume fraction of the polymer ϕ_2 ,

$$G_N^0 = \phi_2^2 G_N^* \quad (1)$$

where G_N^* is the plateau modulus of the polymer. Note that G_N^* is related to the molecular weight of entanglement spacings, M_e :

$$G_N^* = \rho RT/M_e \quad (2)$$

where ρ is the density, R is the universal gas constant, and T is the absolute temperature. Assuming that the polystyrene microdomains in the block copolymer may be regarded as filler dispersed in a continuous polydiene matrix, Holden⁹ estimated the value of G_N^* for ABA-type block copolymers, using the following expression:¹⁰

$$G_N^* = (\rho RT/M_e)(1 + 2.5C + 14.1C^2) \quad (3)$$

where C is the concentration of filler, which in this case is the concentration of polystyrene microdomains in the block copolymer.

When a tackifying resin is added to a block copolymer, often one cannot observe a clear plateau region in plots of G' versus temperature. Kraus and Rollmann⁵ suggested that in such situations, the value of G_N^0 of a mixture consisting of a block copolymer and a tackifying resin can be approximated by the value of G' at the minimum value of loss tangent ($\tan \delta_{min}$).

Class and Chu¹¹ studied the dynamic viscoelastic properties of mixtures of natural rubber (or a synthetic elastomer) and a tackifying resin. They reported that: (1) The molecular weight of the tackifying resin is very important for controlling the compatibility of mixtures, and macrophase separation was observed as the molecular weight of the tackifying resin was increased; (2) The T_g of compatible mixtures of an elastomer and a tackifying resin, as determined by the peak value of $\tan \delta$, can be estimated by the Fox equation:¹²

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \quad (4)$$

where T_g , T_{g1} , and T_{g2} are the peak temperatures of $\tan \delta$ for the mixture and the constituent components, respectively, and w_1 and w_2 are the weight fractions of the constituent components.

It should be pointed out that the studies referred to above have not addressed the important question as to whether or not the mixtures of block copolymer and tackifying resin used were indeed compatible. This is a very important and fundamental question, because the extent of compatibility for a tackifying resin with a block copolymer influences greatly the viscoelastic properties of the

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mixtures and, consequently, the adhesion characteristics of the block copolymer-based pressure-sensitive adhesives.

Thermally-induced transition behavior and phase equilibria in mixtures of a block copolymer and a tackifying resin

Today, it is a well-established fact that when an SB diblock copolymer, SBS or SIS triblock copolymer is heated above the upper (polystyrene) glass transition temperature (T_g), the microdomains of polystyrene will eventually be destroyed and then the block copolymer will form a homogeneous phase. The critical temperature at which the polystyrene microdomains are completely destroyed is often referred to as the "order-disorder transition temperature" (T_c).

An experimental determination or theoretical prediction of T_c is very important to determine optimal processing conditions for a block copolymer or its mixtures with tackifying resins, because the viscosity of a block copolymer becomes very low at and above its T_c . This is due to the fact that at temperatures below T_c , the microdomain structure of polystyrene in a block copolymer acts like a crosslinked network structure, giving rise to a very high viscosity. However, when the microdomain structure of polystyrene is completely destroyed at and above T_c , forming a homogeneous phase, the block copolymer will behave like a homogeneous molten polymer.

In recent years, Helfand and Wasserman¹⁵⁻¹⁷ have developed a statistical thermodynamic theory, and Leibler¹⁸ has also developed a statistical thermodynamic theory, both of which can be used to predict the T_c of block copolymers. Experimentally, Hashimoto and coworkers¹⁷⁻¹⁹ and Roe and coworkers²⁰⁻²³ have investigated the order-disorder transition behavior of SB, SBS or SIS block copolymers and determined their T_c 's, using the small-angle X-ray scattering (SAXS) technique. They reported that the maximum scattered intensity present at room temperature persists well above the glass transition temperature of the polystyrene microdomains, but disappears at a critical temperature (T_c) at which the block copolymer becomes a homogeneous melt. Kraus and Hashimoto²⁴ conducted an experimental SAXS study on pressure-sensitive adhesive systems, and observed that the adhesive showed the same scattering pattern as the block copolymer and that the T_c of the adhesive was lower than that of the block copolymer.

Very recently, Han and coworkers^{25,26} have proposed a rheological technique to determine the T_c of block copolymers, based on dynamic viscoelastic properties measured under isothermal conditions. Basically, the technique calls for logarithmic plots of dynamic storage modulus (G') versus dynamic loss modulus (G''), whereby the T_c of a block copolymer is determined by the temperature at which $\log G'$ versus $\log G''$ plots cease to vary with temperature. Earlier, Han and coworkers²⁷⁻³¹ have shown that when the morphological state of a polymer (a homopolymer, graft copolymer or heterogeneous polymer blend) does not vary with temperature, then $\log G'$ versus $\log G''$ plots become virtually independent of temperature.

When a low molecular-weight homopolymer (e.g., tackifying resin) is mixed with a block copolymer, the mixture can give rise to a complex equilibrium phase diagram, depending upon the extent of compatibility between the two components in the mixture. It is, therefore, very important for one to understand phase equilibria in a pressure-sensitive adhesive system, which consists of a tackifying resin and a block copolymer. Since the chemical structures of tackifying resins are very complex indeed, it would be very useful first to investigate phase equilibria in mixtures of a block copolymer and a homopolymer whose chemical structure is well established; for instance, polydiene, polystyrene or poly(α -methyl styrene) homopolymer. In this regard, it is worth mentioning the recent experimental studies of Roe and coworkers,²¹⁻²³ who investigated phase equilibria in mixtures of SB or SBS block copolymer with polystyrene homopolymer or polybutadiene homopolymer. Independently, Noolandi and coworkers^{22,24} have developed a statistical thermodynamic theory, which allows one to construct phase diagrams for mixtures of a block copolymer and a homopolymer. The phase diagrams constructed theoretically by Whitmore and Noolandi²⁵ look very similar to some of the experimental results of Roe and coworkers.²²

EXPERIMENTAL

Materials

The block copolymers used in this study were: (1) polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) copolymer (KRATON[®] D-1107, Shell Development Company), and (2) polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) copolymer (KRATON[®] D-1102, Shell Development Company). Table I gives the molecular characteristics of the block copolymers investigated. The following two commercial tackifying resins were used: (1) WINGTACK[®] 86 (Goodyear Tire & Rubber Company), and (2) PICCOTAC[®] 95BHT (Hercules Company). The weight-average molecular weights (M_w) of both WINGTACK 86 and PICCOTAC 95BHT were determined by gel permeation chromatography, and the glass transition temperatures (T_g) using differential scanning calorimetry, at a heating rate of 10°C/min. Table II gives a summary of the molecular characteristics and T_g for the tackifying resins investigated. We prepared twenty formulations, by adding different proportions of the tackifying resin (WINGTACK 86 or PICCOTAC 95BHT) to the block copolymer

TABLE I
Molecular characteristics of the block copolymers used

Sample code	Structure	Block molecular weight ($\times 10^{-3}$)	Polystyrene (wt%)	Triblock/diblock ratio
KRATON [®] D-1102	SBS	105-508-105	28	80/20
KRATON [®] D-1107	SIS	105-1201-105	15	80/20

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TABLE II
Molecular characteristics of the tackifying resins used

Sample code	Structure	\bar{M}_w	\bar{M}_w/\bar{M}_n	$T_g(^{\circ}\text{C})$
WINGTACK® 86	Modified polyterpene	1800	1.7	42
PICCOTAC® 95BHT	Piperylene	1100	1.7	43

TABLE III
Summary of the mixtures investigated

Block copolymer	Tackifying resin	Blend ratio
KRATON® 1102	WINGTACK® 86	90/10; 70/30; 50/50; 30/70; 10/90
KRATON® 1102	PICCOTAC® 95BHT	90/10; 70/30; 50/50; 30/70; 10/90
KRATON® 1107	WINGTACK® 86	90/10; 70/30; 50/50; 30/70; 10/90
KRATON® 1107	PICCOTAC® 95BHT	90/10; 70/30; 50/50; 30/70; 10/90

(KRATON 1102 or KRATON 1107). Table III gives a summary of the formulations used in the present investigation.

In the present investigation, an attempt was made to elucidate the structure of WINGTACK 86 and PICCOTAC 95BHT, using infrared (IR) spectroscopy and ^1H nuclear magnetic resonance (NMR) spectroscopy. Based on the IR and NMR data, we have concluded that PICCOTAC 95BHT is an aliphatic hydrocarbon with cyclic structures, and WINGTACK 86 contains aliphatic hydrocarbons and poly(α -methyl styrene).

Sample preparation

Samples for viscoelastic measurements were prepared by first dissolving a predetermined amount of block copolymer and tackifying resin in toluene (10 wt% solid in solution) in the presence of an antioxidant (IRGANOX® 1010, Ciba-Geigy Group) and then slowly evaporating the solvent. The evaporation of solvent was carried out initially in open air at room temperature for a week and then in a vacuum oven at 40°C for three days. The last trace of solvent was removed by drying the samples in a vacuum oven at an elevated temperature by gradually raising the oven temperature up to 110°C. The drying of the samples was continued until there was no further change in weight. Finally, the samples were annealed at 130°C for 10 hours. The formulations employed in this investigation are given in Table III.

Measurement of dynamic viscoelastic properties

A Dynamic Mechanical Spectrometer (Rheometrics Inc.) in the parallel plate mode (8 mm diameter plates with a 2 mm gap) was used to take temperature scans of block copolymer and its mixtures with PICCOTAC 95BHT or WINGTACK 86. From temperature scans made from about -100 to 140°C at a

fixed angular frequency (ω) of 10 rad/s, the dynamic storage modulus (G'), dynamic loss modulus (G''), and loss tangent ($\tan \delta$) defined as G''/G' were plotted against temperature T . From the measurements, values of the plateau modulus (G_N^0) were determined from the plots of G' versus T at which $\tan \delta$ showed a minimum, i.e., values of G' at $\tan \delta_{\min}$.

A Model R16 Weissenberg Rheogoniometer (Sangamo Control Inc.) in the cone-and-plate mode (25 mm diameter plate and 4-degree cone angle with a 160- μ m gap) was used to measure G' and G'' as a function of ω at various temperatures for mixtures of KRATON 1102 (or KRATON 1107) with WINGTACK 86 and with PICCOTAC 95BHT. The purpose of this experiment was to investigate the effect of tackifying resins (WINGTACK 86 and PICCOTAC 95BHT) on the thermally-induced order-disorder transition behavior of the block copolymer, using $\log G'$ versus $\log G''$ plots.

Piezoelectric sorption measurement

The piezoelectric quartz crystal sorption technique was used to determine the interaction parameter χ of the tackifying resin (WINGTACK 86 or PICCOTAC 95BHT) in polybutadiene (PB) homopolymer or polyisoprene (PI) homopolymer. This experimental technique has been successfully used to determine the solubility of a gas or a volatile liquid at elevated temperatures in a polymer^{34,35} and to determine the interaction parameters χ for pairs of polymers.^{36,37}

The apparatus used in this investigation was essentially the same as that described by Harris.³⁷ Briefly mentioned, a quartz crystal with a resonance frequency of approximately 7 MHz was used to determine the amount of solvent sorbed in a polymer sample under a given solvent partial pressure. A polymer solution of approximately 1 wt% was prepared by dissolving the polymer in chloroform. Toluene was chosen as the solvent probe, since toluene had already been used as a solvent in the preparation of the block copolymer/resin mixtures for rheological measurements. All sorption measurements were made at 25°C. The details about the construction of the apparatus and the physical principles involved are referred to in the doctoral dissertation of Harris.³⁷

Turbidity measurements

As will be shown below, the determination of T_i by rheological measurements enables us to construct a phase diagram, as long as the tackifying resin added to a block copolymer does not form a separate phase and the T_i of the block copolymer decreases with increasing amounts of tackifying resin. In the present investigation we have found that mixtures of KRATON 1102 and PICCOTAC 95BHT at certain blend compositions showed evidence of *macrophase* separation at room temperature. Therefore, in order to construct a phase diagram for this system, we conducted turbidity measurements, basically a hot-stage microscope attached to a programmable temperature controller and a laser light source. This device enabled us to take photomicrographs of the sample as the temperature was

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raised from room temperature to about 200°C, at which point the sample showed evidence of thermal degradation.

RESULTS AND DISCUSSION

Viscoelastic behavior of block copolymer-based pressure-sensitive adhesives

Plots of $\log G'$ and $\tan \delta$ versus temperature are given in Figure 1 for mixtures of KRATON 1107 and WINGTACK 86, and in Figure 2 for mixtures of KRATON 1107 and PICCOTAC 95BHT. It can be seen in these figures, over the concentration range investigated, that the addition of WINGTACK 86 or PICCOTAC 95BHT to KRATON 1107 decreased the plateau modulus G'_p , which, in the present case, is approximated by the value of G' at the minimum value of the loss tangent, i.e., by the value of $G'(\tan \delta_{min})$. Note in Figures 1 and 2 that the peak of $\tan \delta$ in the lower transition region, representing the T_g of the polyisoprene phase in KRATON 1107, is shifted toward higher temperatures as the amount of tackifying resin in the mixture is increased. This is a clear indication that the tackifying resins, WINGTACK 86 and PICCOTAC 95BHT, are compatible with the polyisoprene midblock of KRATON 1107 over the concentration range investigated.

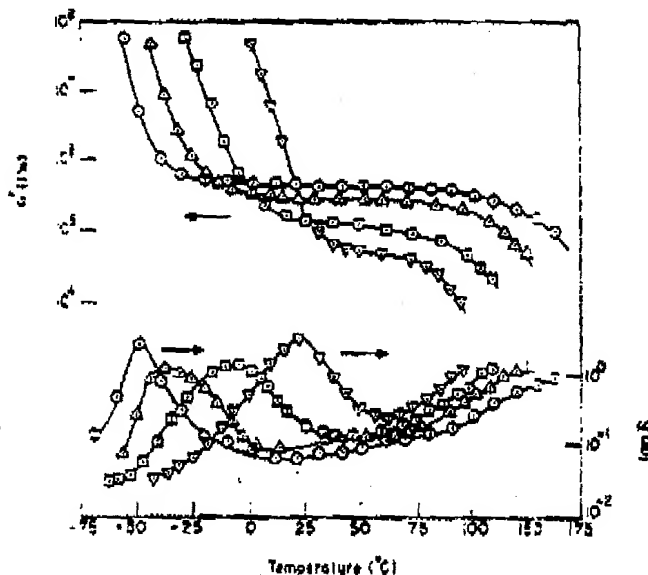


FIGURE 1. Log G' and log $\tan \delta$ versus temperature: (○) KRATON 1107; (Δ) 70/30 KRATON 1107/WINGTACK 86; (□) 50/50 KRATON 1107/WINGTACK 86; (◇) 30/70 KRATON 1107/WINGTACK 86.

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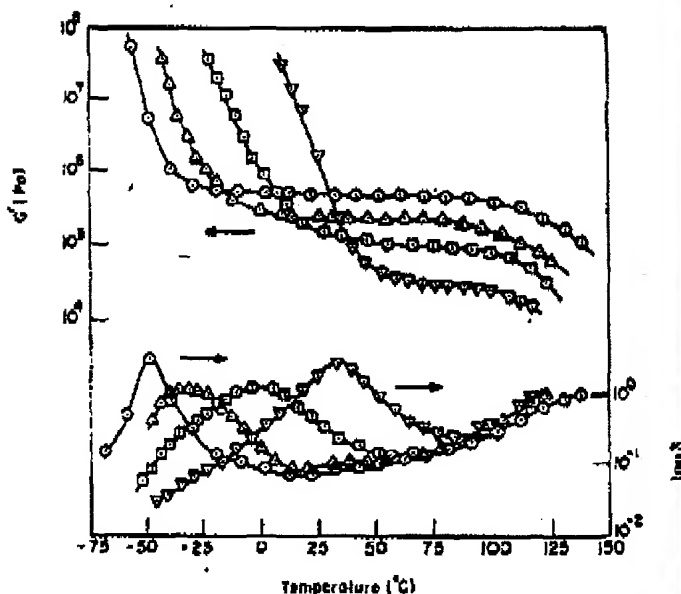


FIGURE 2. Log G' and log $\tan \delta$ versus temperature: (○) KRATON 1107; (△) 70/30 KRATON 1107/PICCOTAC 95BHT; (□) 50/50 KRATON 1107/PICCOTAC 95BHT; (▽) 30/70 KRATON 1107/PICCOTAC 95BHT.

The experimentally determined values of T_g , read off from Figures 1 and 2, are given in Table IV for mixtures of KRATON 1107 and WINGTACK 86, and mixtures of KRATON 1107 and PICCOTAC 95BHT. Figure 3 gives plots of the reciprocal of T_g (absolute temperature) versus weight fraction of tackifying resin, in which the solid line represents the prediction given by Eq. (4) (see Table II for the T_g 's of the tackifying resins). It can be seen that the experimentally obtained T_g values follow closely the theoretical predictions.

TABLE IV
Glass transition temperature (T_g) for mixtures of
KRATON 1107 and tackifying resin

Material	T_g (°C)
(a) KRATON 1107/WINGTACK 86	
100/0	-50
70/30	-34
50/50	-4
30/70	26
(b) KRATON 1107/PICCOTAC 95BHT	
100/0	-50
70/30	-30
50/50	0
30/70	32

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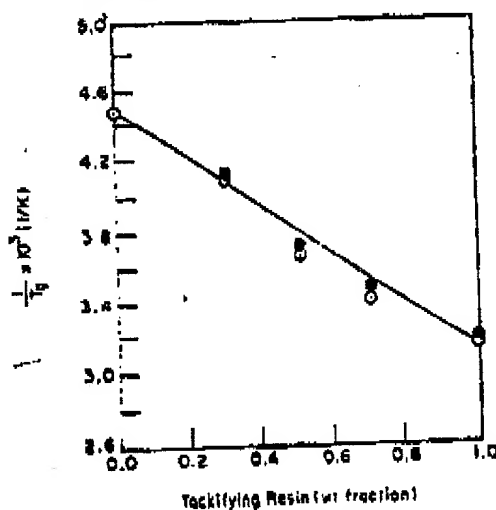


FIGURE 3 $1/T_g$ versus weight fraction of tackifying resin: (○) KRATON 1107/PICCOTAC 95BHT; (●) KRATON 1107/WINGTACK 86 mixtures.

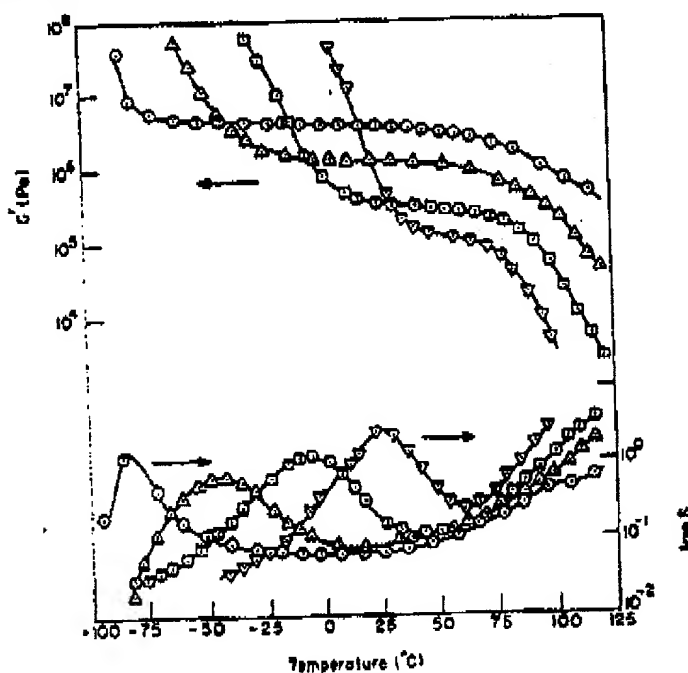


FIGURE 4 Log Q' and log $\tan \delta$ versus temperature: (○) KRATON 1102; (Δ) 70/30 KRATON 1102/WINGTACK 86; (◻) 50/50 KRATON 1102/WINGTACK 86; (◊) 30/70 KRATON 1102/WINGTACK 86.

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On the basis of the experimental observations made above, that $G'(\tan \delta_{\min})$ of KRATON 1107 decreases and the T_g of the polyisoprene phase in KRATON 1107 increases with increasing amount of WINGTACK 86 or PICCOTAC 95BHT, it can be concluded that these two tackifying resins are equally compatible with KRATON 1107, over the concentration range investigated.

Plots of $\log G'$ and $\tan \delta$ versus temperature are given in Figure 4 for mixtures of KRATON 1102 and WINGTACK 86, and in Figure 5 for mixtures of KRATON 1102 and PICCOTAC 95BHT. Figure 6 gives plots of the reciprocal of T_g (absolute temperature) versus weight fraction of WINGTACK 86 for mixtures of KRATON 1102 and WINGTACK 86. In these figures we observe some significant differences in the effect of the respective tackifying resins on the viscoelastic behavior of KRATON 1102, namely: (1) over the concentration range investigated the $G'(\tan \delta_{\min})$ of KRATON 1102 decreased with increasing amount of WINGTACK 86, whereas the $G'(\tan \delta_{\min})$ of KRATON 1102 initially decreased and then increased with increasing amount of PICCOTAC 95BHT; (2) the peak of $\tan \delta$ in the lower transition region, representing the T_g of the polybutadiene phase in KRATON 1102, is shifted steadily to higher temperatures with increasing amount of WINGTACK 86, whereas the peak of $\tan \delta$ in the

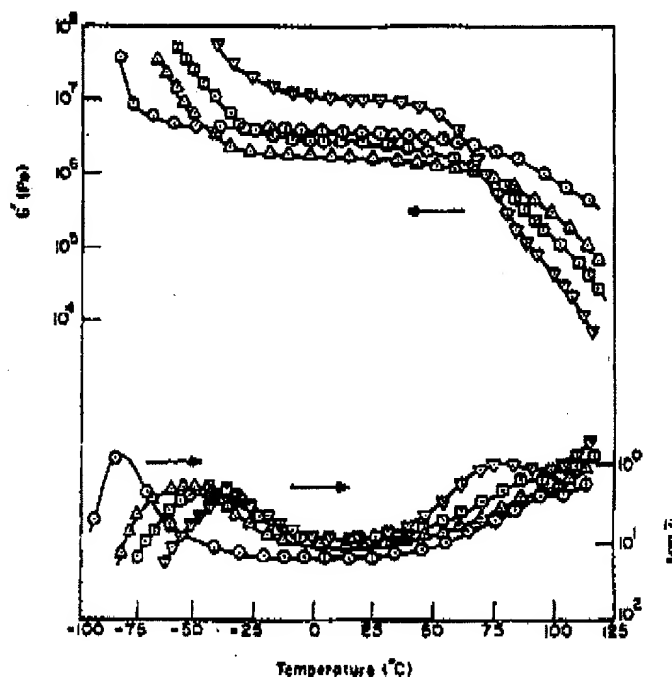


FIGURE 5. $\log G'$ and $\log \tan \delta$ versus temperature: (○) KRATON 1102; (△) 70/30 KRATON 1102/PICCOTAC 95BHT; (□) 50/50 KRATON 1102/PICCOTAC 95BHT; (▽) 30/70 KRATON 1102/PICCOTAC 95BHT.

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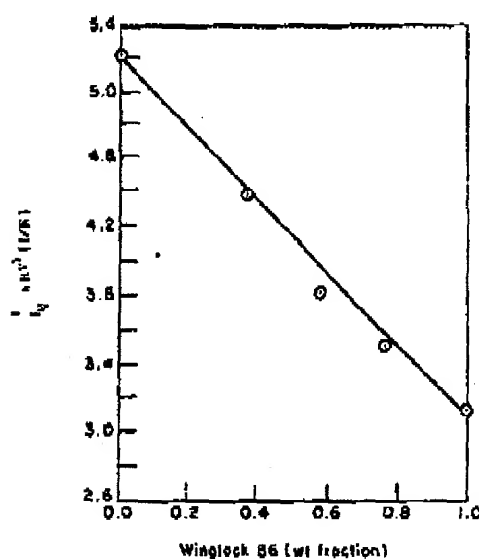


FIGURE 6 $1/T_g$ versus weight fraction of WINGTACK 86 for KRATON 1102/WINGTACK 86 mixtures.

lower transition region of KRATON 1102 is not shifted much as the concentration of PICCOTAC 95BHT in the mixture is increased above 30 wt%. A summary of the values of T_g determined from Figures 4 and 5 are given in Table V.

It is worth pointing out that when a tackifying resin (PICCOTAC 95BHT in the present case) increases the modulus of the block copolymer (KRATON 1102 in the present case), there are two possible reasons: one is that the tackifying resin is associated with the polystyrene domains of the block copolymer, and the other is

TABLE V
Glass transition temperature (T_g) for mixtures of
KRATON 1102 and tackifying resin

Material	T_g (°C)
(a) KRATON 1102/WINGTACK 86	
100/0	-80
70/30	-45
50/50	-6
30/70	23
(b) KRATON 1102/PICCOTAC 95BHT	
100/0	-80
70/30	-55
50/50	-44
30/70	-37

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that the tackifying resin forms a separate phase. As will be shown below, PICCOTAC 95BHT is not compatible with polystyrene homopolymer and, therefore, there is little chance that PICCOTAC 95BHT is associated with the polystyrene domains in KRATON 1102, especially when the amount of PICCOTAC 95BHT in the mixture is as much as 50 wt%. This then leads us to speculate that PICCOTAC 95BHT forms a separate phase. On the basis of the experimental results presented above, it is concluded that WINGTACK 86 is compatible with KRATON 1102, and that PICCOTAC 95BHT is not. Other evidence supporting this conclusion will be presented below.

The interaction parameter χ for an elastomer and a tackifying resin

When presenting the results of viscoelastic behavior, we have noted that the compatibility (or miscibility) of WINGTACK 86 with KRATON 1102 is much greater than that of PICCOTAC 95BHT with KRATON 1102 (compare Figure 4 with Figure 5), and that the compatibility of PICCOTAC 95BHT with KRATON 1107 is much greater than with KRATON 1102 (compare Figure 2 with Figure 5). In order to help understand the physical origins of the experimental observations, we investigated the thermodynamic compatibility of the various mixtures referred to above using the piezoelectric sorption method (see Experimental Section). Since the block copolymers (KRATON 1102 and KRATON 1107) consist of two components, polybutadiene and polystyrene in KRATON 1102, and polyisoprene and polystyrene in KRATON 1107, we decided to determine the interaction parameter χ_{23} between a homopolymer (polybutadiene, polyisoprene or polystyrene) and a tackifying resin (WINGTACK 86 or PICCOTAC 95BHT). For this purpose, we used the following nearly monodisperse homopolymers: (a) polybutadiene with the weight-average molecular weight (\bar{M}_w) 2760; (b) polyisoprene homopolymer with $\bar{M}_w = 75,000$; and (c) polystyrene homopolymer with $\bar{M}_w = 12,200$.

Before proceeding to take the piezoelectric sorption measurements with the various formulations of the pressure-sensitive adhesives that we had prepared, we first checked the accuracy of our measurements with the literature data of Saeki *et al.*,³⁸ by plotting the weight fraction activity coefficient (a_1/w_1) of toluene versus the weight fraction (w_1) of toluene in the polystyrene solution. Figure 7 gives a comparison between the study of Saeki *et al.*³⁸ and this study, which proved to be very satisfactory. Note that the data of Saeki *et al.*³⁸ were also obtained by the piezoelectric sorption method.

Table VI gives a summary of the values of the interaction parameters χ_{23} for the various formulations investigated in the present study. In determining the values of χ_{23} , we have used the Scott theory:³⁹

$$\ln a_1 = \ln \phi_1 + (1 - 1/N_2)\phi_2 + (1 - 1/N_3)\phi_3 + (\chi_{12}\phi_2 + \chi_{13}\phi_3)(1 - \phi_1) - \chi_{23}\phi_2\phi_3 \quad (5)$$

where a_1 is the activity of the solvent, which must be measured in a ternary

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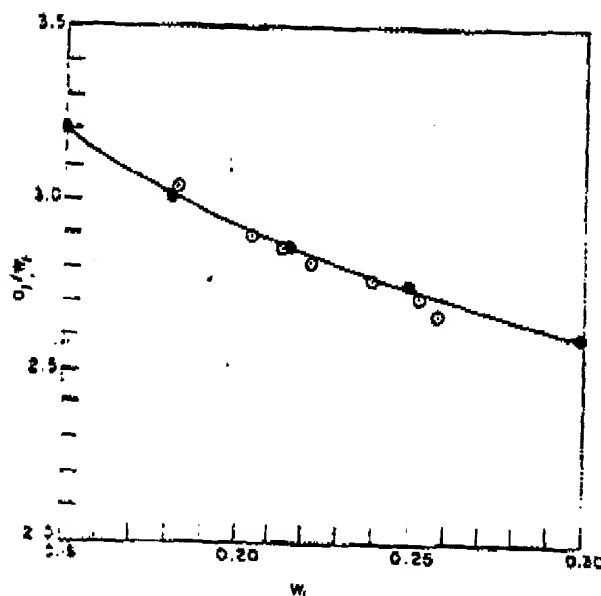


FIGURE 7 a_1/w_1 versus w_1 for polystyrene/toluene mixtures at 25°C: (O) This study; (●) Sasaki *et al.*²⁸ The solid curve drawn is taken from the study of Sasaki *et al.*

solution, ϕ_i ($i = 1, 2, 3$) are the volume fractions of the solvent and two polymers, and N_2 and N_3 are the polymerization indices of components 2 and 3, respectively, which are related to the molar volumes V_2 and V_3 by

$$N_2 = V_2/V_1 \text{ and } N_3 = V_3/V_1 \quad (6)$$

where V_1 is the reference volume, which is usually taken as the molar volume of the solvent in a three-component system. In Eq. (5), χ_{12} is the interaction parameter between polymer 1 (i.e., component 2) and the solvent, and χ_{13} is the interaction parameter between polymer 2 (i.e., component 3) and the solvent, which can be determined from the following expressions:³⁹

$$\ln a_1 = \ln \phi_1 + (1 - 1/N_2)\phi_2 + \chi_{12}\phi_2^2 \quad (7)$$

and

$$\ln a_1 = \ln \phi_1 + (1 - 1/N_3)\phi_3 + \chi_{13}\phi_3^2 \quad (8)$$

Note that the activity of the solvent a_1 , appearing in Eqs. (7) and (8) must be measured in the respective binary systems, i.e., polymer 1/solvent and polymer 2/solvent systems.

In the present investigation, toluene was used as the solvent and the activity of toluene, a_1 , in binary and ternary solutions was determined using the following

TABLE VI
Summary of the values of the interaction parameter χ_{23} for mixtures of a tackifying resin and a homopolymer^a

Weight fraction of polymer	χ_{23}	$-T \Delta S_{mix}$ (cal/cm ³)	ΔH_{mix} (cal/cm ³)	ΔF_{mix} (cal/cm ³)	Comment on film clarity
(a) Polybutadiene/WINGTACK 86 Mixture					
0.674	-0.58	-0.201	-0.702	-0.903	Clear
0.465	-0.41	-0.191	-0.578	-0.769	Clear
0.268	-0.10	-0.136	-0.114	-0.250	Clear
(b) Polyisoprene/WINGTACK 86 Mixture					
0.690	-0.51	-0.196	-0.604	-0.800	Clear
0.305	-0.57	-0.142	-0.695	-0.837	Clear
(c) Polyisoprene/PICCOTAC 95BHT Mixture					
0.747	-0.59	-0.304	-0.614	-0.918	Clear
0.471	-0.04	-0.303	-0.056	-0.359	Clear
0.284	0.11	-0.219	0.129	-0.090	Clear
(d) Polybutadiene/PICCOTAC 95BHT Mixture					
0.714	-0.20	-0.317	-0.224	-0.541	Clear
0.485	0.13	-0.313	0.184	-0.129	Opaque
0.280	0.61	-0.230	0.728	0.498	Opaque
(e) Polystyrene/WINGTACK 86 Mixture					
0.703	-0.47	-0.209	-0.573	-0.782	Clear
0.511	-0.01	-0.202	-0.014	-0.216	Opaque
(f) Polystyrene/PICCOTAC 95BHT					
0.714	0.13	-0.331	0.155	-0.176	Opaque

^a All measurements were conducted at 25°C.

expression:⁴³

$$\alpha_1 = (P_1/P_1^0) \exp[-(B_{11} - v_1)(P_1^0 - P_1)/RT] \quad (9)$$

where P_1 is the system pressure of toluene in the vapor phase, P_1^0 is the saturated vapor pressure of toluene, B_{11} is the second virial coefficient of toluene, v_1 is the molar volume of the solvent, T is the absolute temperature, and R is the universal gas constant. The values of χ_{12} and χ_{13} as determined from Eqs. (7) and (8) were used to determine the values of χ_{23} by Eq. (5).

It should be mentioned that in the use of the piezoelectric sorption method, the weight fraction of the probe solvent w_1 sorbed by a thin polymer film is then calculated using the following relation:⁴¹

$$w_1 = \Delta f' / (\Delta f' + \Delta f_0) \quad (10)$$

where $\Delta f'$ is a decrease in frequency due to the sorption of a probe solvent (toluene in the present study) by the polymer, coated on the quartz crystal, and Δf_0 is a decrease in frequency due to the mass of the polymer, coated on the quartz crystal.

Note that in calculating χ_{23} from Eq. (5), information on the volume fraction of

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solvent ϕ_1 is needed and therefore ϕ_1 must be determined from the experimentally determined w_1 , using information on the specific volume at a desired temperature. When examining Eqs. (5)–(8), it becomes clear that a small error in the values of ϕ_1 can significantly affect the computed values of χ_{12} and χ_{13} , and hence values of χ_{23} .

At this juncture, the magnitude of errors involved must be mentioned in the determination of the interaction parameters χ_{23} using Eq. (5). In calculating w_1 from the frequency measurements using Eq. (10), the values of w_1 were found to vary within $\pm 2\%$, depending on the amount of polymer that was coated on the piezoelectric quartz crystal. This amount of error in w_1 can produce an error of ± 0.02 in the value of χ_{12} (or χ_{13}) for a binary system but can give rise to much larger errors in χ_{23} for a ternary system, since the values of χ_{23} were determined by dividing the difference of two small values, namely, the value of $\ln a_1$ on the left-hand side of Eq. (5) and the value of the terms, excluding the term $\chi_{23}\phi_2\phi_3$, on the right-hand side of Eq. (5), by $\phi_2\phi_3$. Note that values of ϕ_2 and ϕ_3 are always less than 1. Therefore, small errors in ϕ_2 and ϕ_3 can significantly affect the final values of χ_{23} as determined from Eq. (5). In the present investigation, a variation in the value of χ_{23} within ± 0.20 can be expected when the error in w_1 is within $\pm 2\%$.

The following observations are worth noting on the values of χ_{23} given in Table VI. (1) For mixtures of polybutadiene homopolymer and WINGTACK 86, the values of χ_{23} are negative over the concentration range of WINGTACK 86 investigated and that χ_{23} moves toward a positive value with increasing concentration of WINGTACK 86 in the mixture. The negative values of χ_{23} observed for the mixtures of polybutadiene homopolymer and WINGTACK 86 over the concentration range investigated seem to suggest that WINGTACK 86 is compatible with KRATON 1102. This, then, explains why in dynamic viscoelastic measurements the T_g of the polybutadiene phase in KRATON 1102 shifted toward higher temperatures (see Figure 4); (2) For mixtures of polyisoprene homopolymer and WINGTACK 86, the values of χ_{23} are negative over the concentration range of WINGTACK 86 investigated, indicating that WINGTACK 86 is compatible also with KRATON 1107. The negative values of χ_{23} observed for the mixtures seem to explain why the T_g of the polyisoprene phase in KRATON 1107 shifted toward higher temperatures as the amount of WINGTACK 86 in the mixture increased (see Figure 1); (3) For mixtures of PICCOTAC 95BHT with polyisoprene or polybutadiene homopolymer, the value of χ_{23} remains negative in the polyisoprene/PICCOTAC 95BHT mixtures containing up to about 50 wt% of PICCOTAC 95BHT, but becomes slightly positive when the PICCOTAC 95BHT increases to about 70 wt%.

Within the uncertainty limits of the errors involved in the analysis of the piezoelectric sorption data described above, for all intents and purposes the 30/70 polyisoprene/PICCOTAC 95BHT mixture can be considered to be compatible. This observation seems to explain why the addition of PICCOTAC 95BHT to KRATON 1107 increased the T_g of the polyisoprene phase and lowered the plateau modulus of KRATON 1107 (see Figure 2). Note, however, that the

value of χ_{23} is negative for the 70/30 polybutadiene/PICCOTAC 95BHT mixture, but becomes positive for the 50/50 and 30/70 polybutadiene/PICCOTAC 95BHT mixtures. The concentration of PICCOTAC 95BHT at which χ_{23} is negative is much lower in the mixtures with polybutadiene homopolymer than with polyisoprene homopolymer, meaning that the miscibility limits (or extent of compatibility) of PICCOTAC 95BHT with KRATON 1102 would be much lower than with KRATON 1107. This observation now explains why in the 50/50 and 30/70 KRATON 1102/PICCOTAC 95BHT mixtures, the plateau modulus increased while the T_g of the rubbery polydiene phase in the KRATON 1102/PICCOTAC 95BHT mixtures hardly increased, for amounts of PICCOTAC 95BHT in the mixture-above 50 wt% (see Figure 5); (4) For mixtures of polystyrene homopolymer with WINGTACK 86 or PICCOTAC 95BHT, at about the same level of tackifying resin in the mixture, the value of χ_{23} is *negative* for the polystyrene/WINGTACK 86 mixture, while it is *positive* for the polystyrene/PICCOTAC 95BHT mixture, which means that WINGTACK 86 is compatible with polystyrene within the concentration range investigated. This observation is not surprising, in view of the fact that WINGTACK 86 contains a significant amount of poly(α -methyl styrene), as detected by IR spectroscopy. And yet, since the major portion of WINGTACK 86 consists of aliphatic hydrocarbons, it is believed to have fairly limited miscibility with polystyrene homopolymer. Thus, the addition of a large amount of WINGTACK 86 to polystyrene homopolymer is expected to give rise to *macrophase separation*.

It should be mentioned that values of the interaction parameter do not necessarily have to be *negative* for a tackifying resin to be compatible with a block copolymer, because the entropic contribution ($T\Delta S_{mix}$) of the tackifying resin, which is negative, can offset a positive value of the enthalpic contribution (ΔH_{mix}) when the value of the interaction parameter is positive, giving rise to a negative value for the free energy of mixing, ΔF_{mix} . This can be illustrated best by looking at the values of $-T\Delta S_{mix}$, ΔH_{mix} , and ΔF_{mix} , given in Table VI. Note that the value of ΔH_{mix} and $-T\Delta S_{mix}$ given in Table VI were determined, using the Flory-Huggins theory:^{42,43}

$$\Delta F_{mix} = RT \left(\frac{\phi_1}{V_1} \ln \phi_1 + \frac{\phi_2}{V_2} \ln \phi_2 + \frac{\chi}{V_r} \phi_1 \phi_2 \right) \quad (11)$$

where ϕ_i ($i = 1, 2$) are the volume fractions, and V_i ($i = 1, 2$) are the molar volumes, of the constituent components, V_r is the reference volume of one of the components (i.e., the volume of a segment or a lattice), R is the universal gas constant, T is the absolute temperature, and χ is the interaction parameter which is equivalent to χ_{23} in Eq. (5). It can be seen that when the contribution of $-T\Delta S_{mix}$ outweighs the contribution of ΔH_{mix} , the value of ΔF_{mix} becomes negative (i.e., the mixture is compatible) even when the value of χ_{23} is slightly positive.

Let us now examine whether or not the use of the solubility parameter δ would give the same information as that of the interaction parameter χ , in predicting the

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BHT mixture, PICCOTAC 95BHT is negative is than with pol- or extent of the much lower the 50/50 and eau modulus the KRATON PICCOTAC mixtures of BHT, at about is negative for tive for the OTACK 86 is tigated. This 86 contains a spectroscopy. s of aliphatic h polystyrene TACK 86 to paration. neter do not e with a block ckifying resin, ation (ΔH_{mix}) to a negative est by looking Note that the ed. using the

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compatibility of a tackifying resin with a block copolymer. For this purpose, let us compare the compatibilities of PICCOTAC 95BHT with polyisoprene and polybutadiene, respectively. It can be seen in Table VI that, over the concentration range investigated, the values of χ_{23} for PICCOTAC 95BHT and polyisoprene homopolymer are negative for PICCOTAC 95BHT concentrations up to about 50 wt% and then become slightly positive at higher concentrations. Nevertheless, the values of ΔF_{mix} are negative over the entire range of PICCOTAC 95BHT concentrations investigated. On the other hand, for the PICCOTAC 95BHT/polybutadiene mixtures, the values of χ_{23} are negative for PICCOTAC 95BHT concentration up to about 30 wt% but increase rapidly, becoming positive, as the concentration is increased further, and values of ΔF_{mix} are positive at concentrations of PICCOTAC 95BHT above approximately 50 wt%. This observation now explains the limited compatibility of PICCOTAC 95BHT with KRATON 1102, observed in the viscoelastic measurements displayed in Figure 5.

The chemical structure of PICCOTAC 95BHT is not clearly known to us, but it is reported that piperylene is a major monomer for PICCOTAC 95BHT.³ Let us then use piperylene to evaluate the solubility parameter δ of PICCOTAC 95BHT. Using the group contribution method, the value of δ for PICCOTAC 95BHT is estimated to be $8.20 \text{ (cal/cm}^3)^{1/2}$ using the data of Fedors,⁴⁴ $8.33 \text{ (cal/cm}^3)^{1/2}$ using the data of van Krevelen,⁴⁵ $7.76 \text{ (cal/cm}^3)^{1/2}$ using data of Small,⁴⁶ $8.16 \text{ (cal/cm}^3)^{1/2}$ using the data of van Krevelen,⁴⁷ and $7.92 \text{ (cal/cm}^3)^{1/2}$ using the data of Hoy.⁴⁸ The average of the five values is $8.09 \text{ (cal/cm}^3)^{1/2}$. Since the values of the solubility parameter for polyisoprene and polybutadiene are 8.50 and $8.55 \text{ (cal/cm}^3)^{1/2}$, respectively, the difference in solubility parameters between PICCOTAC 95BHT and polyisoprene, $(\delta_{PI} - \delta_{PIC95})$, is $0.41 \text{ (cal/cm}^3)^{1/2}$, and the difference in solubility parameters between PICCOTAC 95BHT and polybutadiene, $(\delta_{PB} - \delta_{PIC95})$, is $0.46 \text{ (cal/cm}^3)^{1/2}$. When these values are used for different values of ϕ_1 (volume fraction of PICCOTAC 95BHT), we cannot explain why PICCOTAC 95BHT is compatible with KRATON 1107, while it becomes incompatible (i.e., forms a separate phase) with KRATON 1102. Therefore, we conclude that the solubility parameter has very limited usefulness in predicting compatibility between a tackifying resin and a block copolymer.

Phase diagrams of block copolymer-based pressure-sensitive adhesives

In the development of formulas for block copolymer-based pressure-sensitive adhesives, it is important to have phase diagrams available. The construction of a phase diagram for mixtures of a block copolymer and a tackifying resin is not as easy as that for binary mixtures of simple liquids, because block copolymers have microdomain structures at temperatures below a certain critical value, referred to above as the order-disorder transition (or microphase separation transition) temperature T_c . As mentioned above, the size of the microdomains is too small to be detected by ordinary optical microscopy, and thus the determination of T_c for a block copolymer or its mixtures with a homopolymer has often been done by

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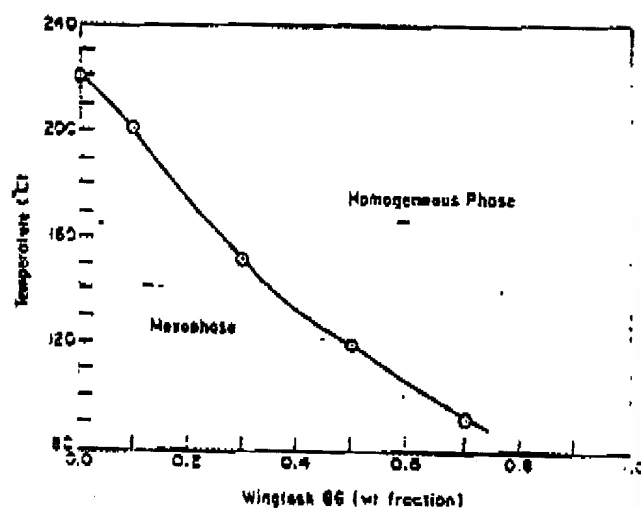


FIGURE 8 Phase diagram for KRATON 1102/WINGTACK 86 mixtures.

small-angle X-ray scattering.¹⁷⁻²⁴ In the present investigation, however, we have used a rheological technique, introduced very recently by us,^{23,24} to determine the values of T , for block copolymer and its mixtures with a tackifying resin.

Figure 8 gives a phase diagram for mixtures of KRATON 1102 and WINGTACK 86, and Figure 9 gives a phase diagram for mixtures of KRATON 1107 and WINGTACK 86. Note in Figures 8 and 9 that the region below the solid

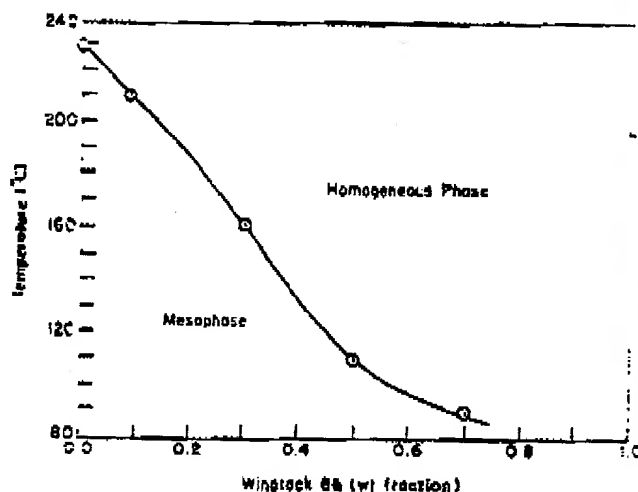


FIGURE 9 Phase diagram for KRATON 1107/WINGTACK 86 mixtures.

FIG 1
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curve represents the mesophase (mixtures of the block copolymer and the tackifying resin) and that the region above the solid curve represents the mixtures, where the block copolymer and the tackifying resin form a homogeneous, single phase.

The circular symbols in Figures 8 and 9 are values of temperature (i.e., T_g), which were determined from logarithmic plots of dynamic storage modulus G' versus dynamic loss modulus G'' for the block copolymer (KRATON 1102 or KRATON 1107) and its mixtures with WINGTACK 86. In order to illustrate the method used to determine T_g , let us look at Figure 10, $\log G'$ versus $\log G''$ plots for KRATON 1102. It can be seen in Figure 10 that the $\log G'$ versus $\log G''$ plots do not change with temperature at 220°C and above. According to the criterion suggested in our previous papers,^{25,26} the lowest temperature at which $\log G'$ versus $\log G''$ plots cease to vary with temperature is the T_g , at which point the microdomain structures in the block copolymer dissolve completely. Figure 11 gives $\log G'$ versus $\log G''$ plots for the 90/10 KRATON 1102/WINGTACK 86 mixture, and Figure 12 for the 70/30 KRATON 1102/WINGTACK 86 mixture. It

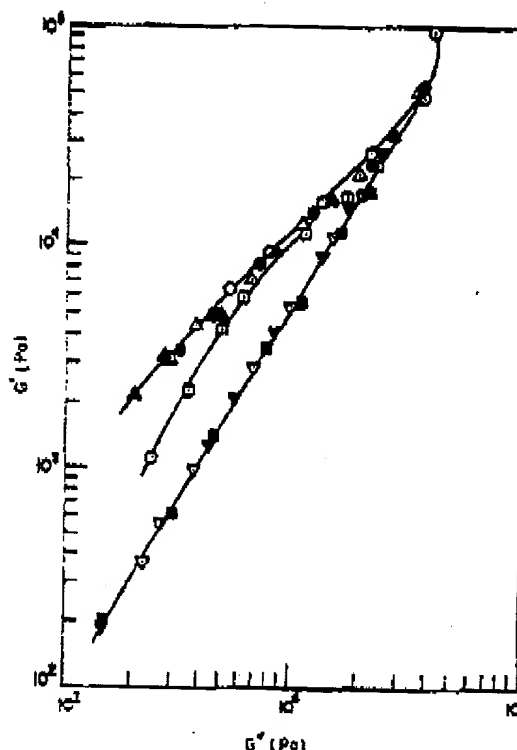


FIGURE 10 $\log G'$ versus $\log G''$ plots for KRATON 1102 at various temperatures (°C): (○) 160; (●) 180; (△) 190; (▲) 200; (◻) 210; (■) 220; (▽) 230; (▼) 240.

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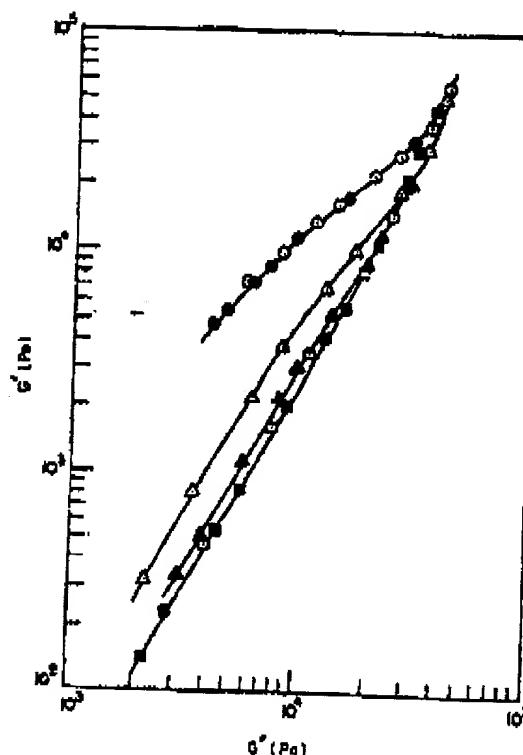


FIGURE 11 Log G' versus log G'' plots for the 90/10 KRATON 1102/WINGTACK 86 mixture at various temperatures ($^{\circ}\text{C}$): (\odot) 140; (\bullet) 170; (Δ) 180; (\triangle) 190; (\square) 200; (\blacksquare) 210.

can be seen in Figures 11 and 12 that T_i decreased as the concentration of WINGTACK 86 in the mixture increased. Due to space limitations here, log G' versus log G'' plots for mixtures of other blend compositions are not presented, but a summary of the T_i 's determined are given in Table VII. It is of interest to observe in Figure 8 that the temperature at which the microdomain structures dissolve completely decreases steadily with increasing amounts of WINGTACK 86 in KRATON 1102. Based on the information given in Figure 9, a similar observation can be made for the KRATON 1107/WINGTACK 86 mixtures.

It should be mentioned that when the light-scattering experiments and hot-stage microscopy were performed for the mixtures of WINGTACK 86 with KRATON 1102 or KRATON 1107, and for the mixtures of PICCOTAC 95BHT with KRATON 1107, no evidence of the occurrence of *macrophase* separation over the temperature range investigated was obtained. However, there was evidence of *macrophase* separation occurring in certain compositions of the

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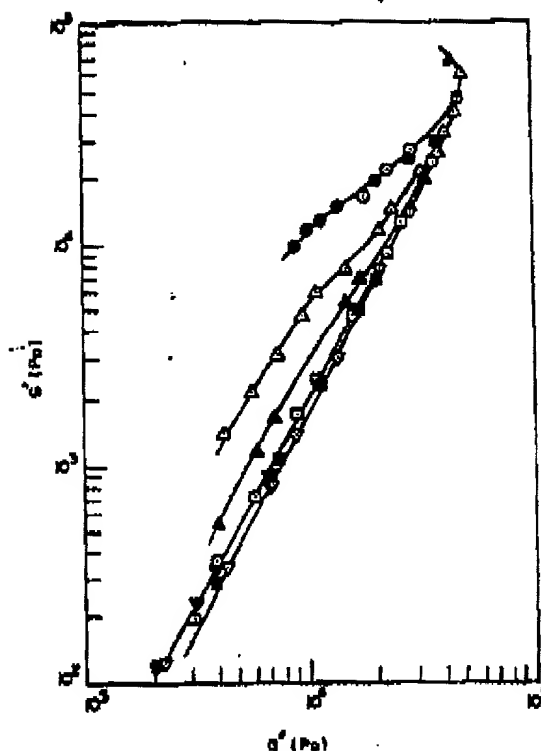


FIGURE 12 Log G' versus log G'' plots for the 70/30 KRATON 1102/WINGTACK 86 mixture at various temperatures ($^{\circ}\text{C}$): (\odot) 100; (\bullet) 110; (Δ) 120; (\triangle) 140; (\square) 150; (\blacksquare) 160; (∇) 180; (\blacktriangledown) 200.

TABLE VII

Summary of the order-disorder transition temperature (T_i) for mixtures of a block copolymer and a tackifying resin

Material	T_i ($^{\circ}\text{C}$)
KRATON 1102	220
KRATON 1102/WINGTACK 86 = 90/10	200
KRATON 1102/WINGTACK 86 = 70/30	150
KRATON 1102/WINGTACK 86 = 50/50	120
KRATON 1102/WINGTACK 86 = 30/70	90
KRATON 1107	230
KRATON 1107/WINGTACK 86 = 90/10	210
KRATON 1107/WINGTACK 86 = 70/30	160
KRATON 1107/WINGTACK 86 = 50/50	110
KRATON 1107/WINGTACK 86 = 30/70	90
KRATON 1107/PICCOTAC 95BHT = 70/30	200
KRATON 1107/PICCOTAC 95BHT = 50/50	180
KRATON 1107/PICCOTAC 95BHT = 30/70	160
KRATON 1102/PICCOTAC 95BHT = 90/10	200

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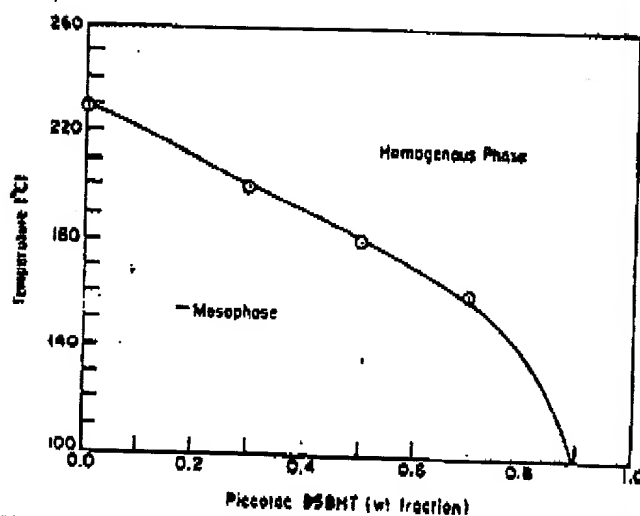


FIGURE 13 Phase diagram for KRATON 1107/PICCOTAC 95BHT mixtures.

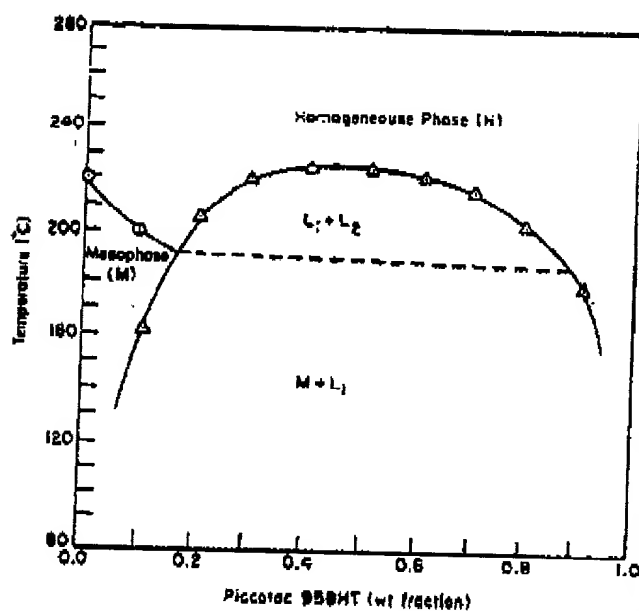


FIGURE 14 Phase diagram for KRATON 1102/PICCOTAC 95BHT mixtures.

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mixtures of PICCOTAC 95BHT with KRATON 1102 over the temperature range investigated.

Figure 13 gives a phase diagram for the KRATON 1107/PICCOTAC 95BHT mixtures, and Figure 14 gives a phase diagram for the KRATON 1102/PICCOTAC 95BHT mixtures. These phase diagrams were constructed using information obtained from both the rheological technique and hot-stage microscopy. The phase diagram for the KRATON 1107/PICCOTAC 95BHT mixtures looks very similar to the phase diagrams for the KRATON 1102/WINGTACK 86 mixtures (see Figure 8) and KRATON 1107/WINGTACK 86 mixtures (see Figure 9). But the phase diagram for the KRATON 1102/PICCOTAC 95BHT mixtures looks much more complex. Note in Figure 14 that the circular symbols on the curve separating the mesophase and the homogeneous phase are the values of T , determined from $\log G'$ versus $\log G''$ plots and that the triangular symbols represent the phase boundary as determined by hot-stage microscopy. Due to the limited magnifications available, the phase boundary determined by the hot-stage microscope is considered to be approximate. Note further in Figure 14 that region $M + L_1$ represents the mixtures of microphase separated KRATON 1102 (denoted by M) and macrophase separated PICCOTAC 95BHT (denoted by L_1), and that region $L_1 + L_2$ represents two-phase mixtures of PICCOTAC 95BHT (denoted by L_1) and completely disordered KRATON 1102 (denoted by L_2). It can be concluded from these figures that PICCOTAC 95BHT has a very limited solubility in KRATON 1102, as compared with WINGTACK 86. This conclusion supports the validity of the hypotheses made above when we examined the viscoelastic behavior of the mixtures.

Processability of block copolymer-based pressure-sensitive adhesives

Information on viscosity is very valuable for determining the processability of block copolymer-based pressure-sensitive adhesives. According to Cox and Merz,⁴⁹ only when linear viscoelastic data are available do plots of complex viscosity $|\eta^*(\omega)|$ versus angular frequency ω become very useful in predicting the relationship between steady shear viscosity $\eta(\dot{\gamma})$ and shear rate $\dot{\gamma}$. Note that values of $|\eta^*|$ can be calculated using the definition, $|\eta^*(\omega)| = [\eta'(\omega)^2 + \eta''(\omega)^2]^{1/2}$, where $\eta'(\omega)$ is equal to $G'(\omega)/\omega$ and $\eta''(\omega)$ is equal to $G''(\omega)/\omega$.

Figure 15 gives logarithmic plots of $|\eta^*|$ versus ω for the 50/50 KRATON 1102/WINGTACK 86 mixture at the following temperatures: 90, 100, 110, 120, and 140°C. Similar plots are given in Figure 16 for the 50/50 KRATON 1107/WINGTACK 86 mixture at the following temperatures: 100, 110, 130, 140, and 160°C, in Figure 17 for the 50/50 KRATON 1102/PICCOTAC 95BHT mixture at the following temperatures: 120, 130, 140, 150, and 160°C, and in Figure 18 for the 50/50 KRATON 1107/PICCOTAC 95BHT mixture at the following temperatures: 120, 140, 160, 180, and 190°C. It can be seen in Figures 15 to 18 that the $\log |\eta^*|$ versus $\log \omega$ plots exhibit Newtonian behavior at temperatures above its T_g , but yield behavior at temperatures below its T_g (see

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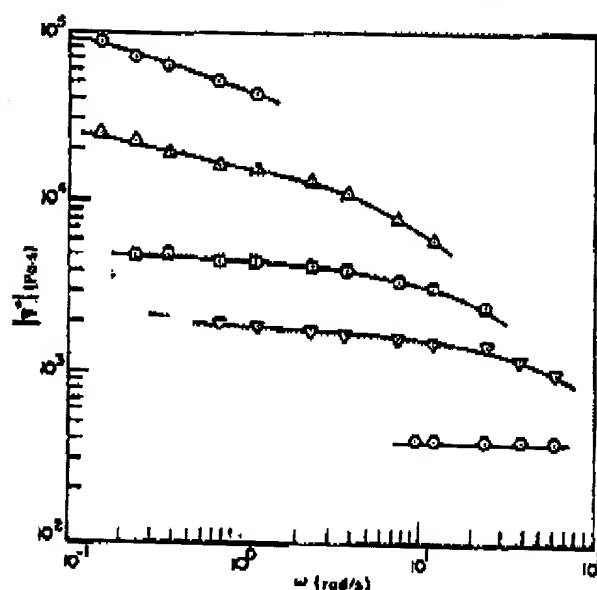


FIGURE 15 Log $[\eta^*]$ versus $\log \omega$ for the 50/50 KRATON 1102/WINGTACK 86 mixture at various temperatures ($^{\circ}\text{C}$): (\circ) 90; (Δ) 100; (\square) 110; (∇) 120; (\odot) 140.

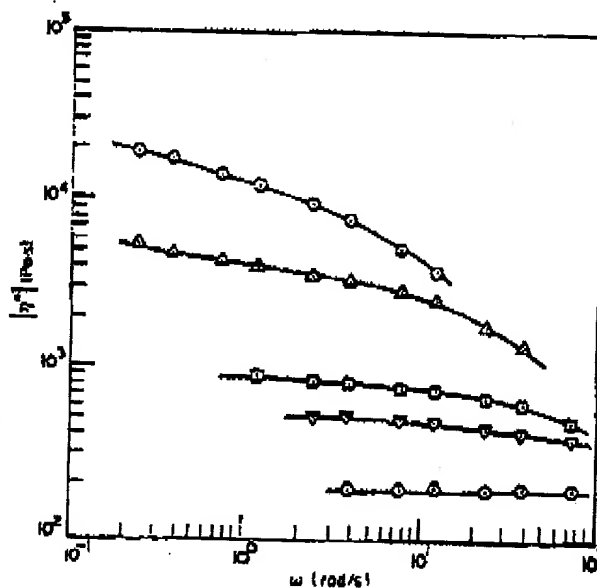


FIGURE 16 Log $[\eta^*]$ versus $\log \omega$ for the 50/50 KRATON 1107/WINGTACK 86 mixture at various temperatures ($^{\circ}\text{C}$): (\circ) 100; (Δ) 110; (\square) 130; (∇) 140; (\odot) 160.

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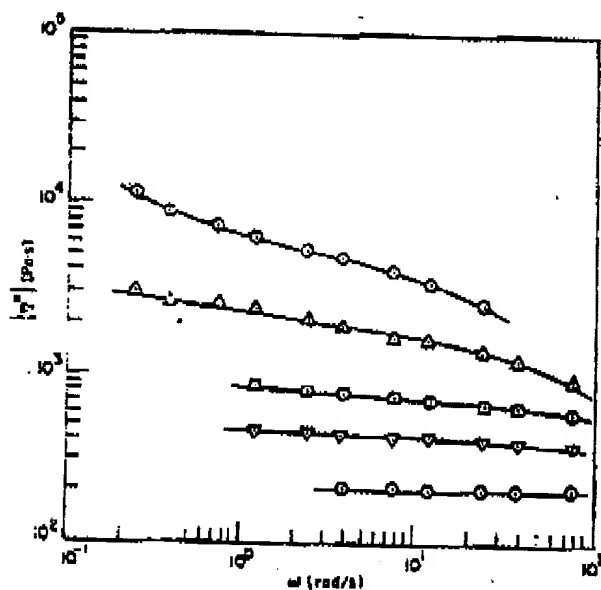


FIGURE 17 Log $|\eta^*|$ versus log ω for the 50/50 KRATON 1102/PICCOTAC 95BHT at various temperatures ($^{\circ}\text{C}$): (\odot) 120; (Δ) 130; (\square) 140; (∇) 150; (\circ) 160.

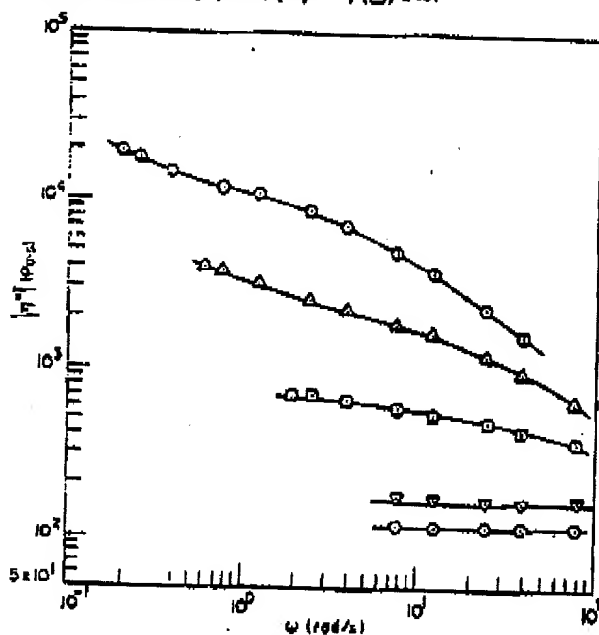


FIGURE 18 Log $|\eta^*|$ versus log ω for the 50/50 KRATON 1107/PICCOTAC 95BHT at various temperatures ($^{\circ}\text{C}$): (\odot) 120; (Δ) 140; (\square) 160; (∇) 180; (\circ) 190.

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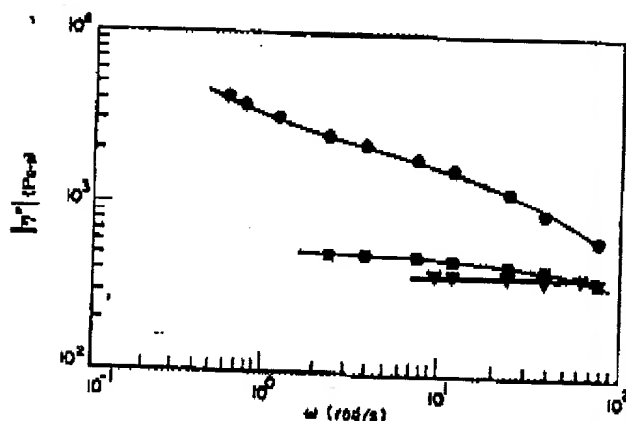


FIGURE 19 Log $|\eta^*|$ versus log ω at 140°C: (●) 50/50 KRATON 1107/PICCOTAC 95BHT; (▲) 50/50 KRATON 1107/WINGTACK 86; (■) 50/50 KRATON 1102/WINGTACK 86.

Table VII and Figure 13 and 14 for values of the T_g of the block copolymer/tackifying resin systems investigated). From the processing point of view, it is highly desirable to have viscosities as low as possible. This, then, suggests to us that the processing temperature chosen should be above the T_g of a given pressure-sensitive adhesive. In this regard, information on the T_g of a pressure-sensitive adhesive is very valuable to determine the optimum processing conditions.

To illustrate the point emphasized above, let us observe the plots of log $|\eta^*|$ versus log ω at 140°C, given in Figure 19, for mixtures containing different tackifying resins at a fixed blend composition, 50/50 block copolymer/tackifying resin mixture. It can be seen in Figure 19 that the viscosities of the 50/50 KRATON 1102/WINGTACK 86 and 50/50 KRATON 1107/WINGTACK 86 mixtures are much lower than the viscosities of the 50/50 KRATON 1107/PICCOTAC 95BHT mixture. Note that the T_g 's of the 50/50 KRATON 1102/WINGTACK 86 and 50/50 KRATON 1107/WINGTACK 86 mixtures are 120°C and 110°C, respectively, which are below the processing temperature 140°C, whereas the T_g of the 50/50 KRATON 1107/PICCOTAC 95BHT mixture is 180°C which is above the processing temperature of 140°C (see Table VII for information on the T_g 's of the block copolymer/tackifying resin mixtures employed). It is then clear why the viscosities of the 50/50 KRATON 1102/WINGTACK 86 and 50/50 KRATON 1107/WINGTACK 86 mixtures are much lower than the viscosities of the KRATON 1107/PICCOTAC 95BHT.

CONCLUDING REMARKS

In this paper we have presented experimental results for the viscoelastic behavior, the Flory-Huggins interaction parameter, and phase diagrams of block

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copolymer-based pressure-sensitive adhesives. It has been found that different experimental techniques produced consistent results regarding the compatibility of a tackifying resin with a block copolymer. We have demonstrated that the use of the Flory-Huggins interaction parameter is much more reliable than the use of the Hildebrand solubility parameter in determining the compatibility for a tackifying resin with a block copolymer. It should be mentioned that in order to determine the interaction parameter for a tackifying resin and a block copolymer using Scott's theory, Eq. (5), together with the piezoelectric sorption method, one must have accurate information on the molar volumes, V_1 and V_2 , of the repeat units of the tackifying resin and the block copolymer. Unfortunately, the chemical structures of most of the tackifying resins in commercial use today are very complex and not clearly understood. Thus, under such circumstances, the accurate determination of the interaction parameter χ_{23} using Eq. (5) would be very difficult, if not impossible. This, then, suggests that, in the future, efforts should be directed towards the elucidation of the chemical structures of tackifying resins.

We have found that values of the interaction parameter χ_{23} for certain mixtures of a tackifying resin and a block copolymer are negative. Earlier, using gas-liquid chromatography, Su *et al.*²⁰ also obtained negative values of χ_{23} in poly(vinyl chloride) (PVC) plasticized by di-n-octyl phthalate (DnOP). Note that in analyzing experimental data to determine values of χ_{23} , they also used Eq. (5). They observed that the value of χ_{23} was negative up to 0.25 volume fraction of DnOP but it became less negative and finally positive at 0.55 volume fraction of DnOP. They then concluded that the compatibility of PVC with DnOP depended upon the composition of the mixtures investigated.

Kraus and Rollmann² reported that a plateau modulus in the vicinity of 3×10^5 Pa gives a satisfactory tack property for applications in pressure-sensitive adhesives. Based on this criterion, we can conclude that the 30/50 and 30/70 KRATON 1107/WINGTACK 86 mixtures (see Figure 1), the 50/50 and 30/70 KRATON 1107/PICCOTAC 95BHT mixtures (see Figure 2), and the 30/70 KRATON 1102/WINGTACK 86 mixture (see Figure 4) may be considered to be effective formulas for pressure-sensitive adhesives. The present study shows that, on an equal weight basis, WINGTACK 86 is more effective in lowering the plateau modulus of KRATON 1107 than that of KRATON 1102. Due to very limited compatibility with KRATON 1102, PICCOTAC 95BHT was found to form a separate phase.

We have constructed phase diagrams of block copolymer-based pressure-sensitive adhesives, using information obtained from both the dynamic viscoelastic measurements and a light scattering method (or hot-stage microscopy).

Acknowledgment

We wish to acknowledge with gratitude that the Shell Development Company supplied us with the block copolymers, KRATON[®] D-1102 and KRATON[®] D-1107, Hercules Incorporated supplied us with PICCOTAC[®] 95BHT, and the Goodyear Tire and Rubber company supplied us with WINGTACK[®] 86 used in this investigation.

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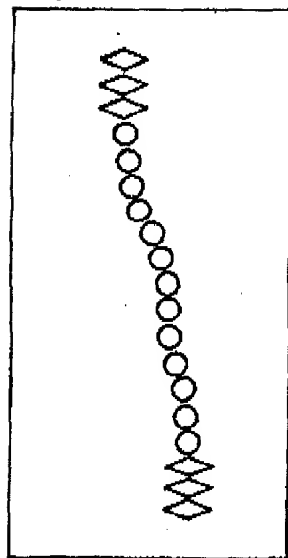
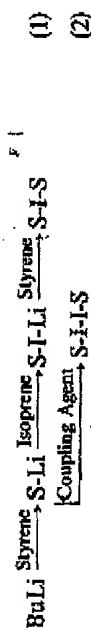


Fig. 11-1. Simplified representation of a thermoplastic rubber molecule.

and the circles represent monomer units in the rubbery midblock. There are two basic classes of thermoplastic rubber. One class consists of block polymers in which the rubbery midblock of the molecule is an unsaturated rubber. The two types of polymers in this class are the polystyrene-polybutadiene-polystyrene (S-B-S) polymers and the polystyrene-polyisoprene-polystyrene (S-I-S) polymers. This class of thermoplastic rubber was first marketed commercially in 1965 by Shell Chemical Company. The second class of thermoplastic rubber consists of block polymers in which the elastomeric midblock is a saturated olefin rubber. The polymers in this class are the polystyrene-poly(ethylene/butylene)-polystyrene (S-EB-S) polymers and the polystyrene-poly(ethylene/propylene)-polystyrene (S-EP-S) polymers. This class of thermoplastic rubber was first marketed commercially in 1972 by Shell Chemical Company.

The usual method of preparation of thermoplastic rubbers is by anionic polymerization in solvent using an alkyl lithium catalyst such as butyllithium. S-B-S and S-I-S type block polymers may be synthesized by two basic routes: sequential polymerization of all three blocks or sequential polymerization of two blocks, followed by coupling. These two processes are illustrated below, the sequential process in Equation (1) and the coupling process in Equation (2), for the preparation of an S-I-S type polymer.



The sequential process results in what is called a linear S-I-S polymer. With the coupling process, use of a difunctional coupling agent gives a linear (S-I)₂ polymer, while use of a multifunctional coupling agent gives a multiarmed (S-I)_n polymer. Usual coupling agents are esters or halogen containing molecules. Literature reports catalytic hydrogenation of S-B-S and S-I-S

Chapter 11

Block Copolymers

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Thermoplastic rubbers of the ABA block copolymer type, where A represents a thermoplastic polystyrene endblock and B represents a rubber midblock of polyisoprene, polybutadiene, or poly(ethylene/butylene), form a useful and versatile group of polymers for pressure-sensitive adhesives.

Because of their unique structure, thermoplastic rubbers offer processing advantages to the adhesive manufacturer as well as providing required performance in a wide range of formulated pressure-sensitive adhesive tape and label products. In preparing solvent-based adhesives, thermoplastic rubbers require no premastication, as they dissolve rapidly in common solvents. Usually finished thermoplastic rubber adhesives can be coated at much higher solids contents than adhesives based on conventional rubbers, as solution viscosities are lower. Also, because these rubbers are thermoplastic, they allow preparation of adhesives which can be mixed and coated as solvent-free, hot melt pressure-sensitive adhesives.

NATURE OF THE BASIC MOLECULE

Architecture

The simplest thermoplastic rubber consists of a rubbery midblock with two plastic polystyrene endblocks. This is pictured schematically in Fig. 11-1 where the diamonds represent monomer units in the polystyrene endblocks

polymers to produce saturated analogues of the S-EB-S and S-EP-S types, respectively.¹

Many variations can be made in the structure of a thermoplastic rubber. Among these are variations in molecular weight, styrene content, monomers used in the polymerization and the number of polymer arms coupled in the coupling reaction. The key requirement for a thermoplastic rubber is that the rubber midblock, having a glass transition temperature T_g well below room temperature, must have terminal endblocks of a hard, glasslike plastic, also having a glass transition temperature well above room temperature. An additional requirement is that the plastic endblocks must be thermodynamically incompatible with the rubber midblock. When these requirements are fulfilled, the polymer can consist of two phases: a continuous rubber phase and a basically discontinuous plastic phase. A highly idealized representation of this phase separated structure is given in Fig. 11-2.

Domains, the plastic endblock phase, are shown in Fig. 11-2 in spherical form. These domains act as crosslinks between the ends of many rubber chains, thereby locking the rubber chains and their inherent entanglements in place. Thus, the thermoplastic rubber behaves like a conventionally vulcanized rubber that contains dispersed reactive filler particles. However, the thermoplastic rubber is physically crosslinked by the plastic endblock domains rather than being chemically crosslinked like a conventionally vulcanized rubber. As such, these physical crosslink sites (domains) can be reversibly unlocked and reformed by various means, i.e., solvation followed by solvent evaporation or through sufficient heating and shearing, then cooling.

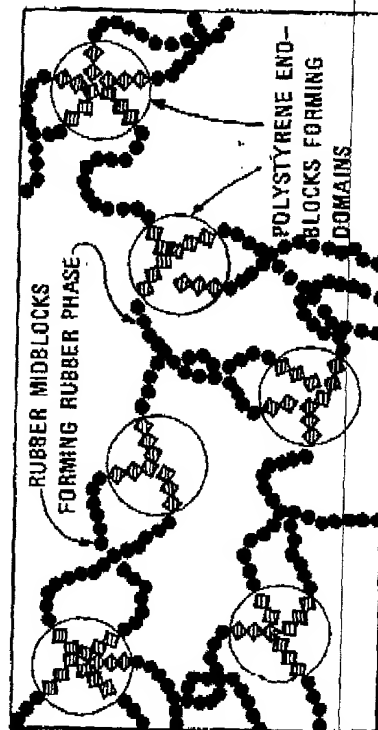


Fig. 11-2. Idealized two-phase network of thermoplastic rubber molecules.

The behavior of thermoplastic rubber is highly dependent on the morphology or geometry of the endblock domains as they are dispersed in the rubber matrix. In commercial thermoplastic rubbers useful for pressure-sensitive adhesives, the endblock phase is present in the smaller proportion and is dispersed in a continuous rubber matrix as suggested by Fig. 11-3. The uniform dispersion of spherical endblock domains shown in this figure (A, spheroids), however, is approached only in carefully prepared laboratory samples, with low endblock phase concentration. Depending on the endblock phase concentration and on actual processing conditions used to prepare a given sample, the geometry or morphology of the dispersed phase may be spheroidal, rodlike, or lamellar as depicted in Fig. 11-3. The existence of these different morphologies has been confirmed by electron micrographs.^{2,3}

In the latter two cases, the endblock phase may extend as a continuous plastic network throughout the rubber matrix. This tends to be the case when the endblock phase concentration is above about 20%w for neat S-B-S thermoplastic rubbers. In this situation, as the sample is stretched, the initial stress is borne by the plastic network, and the stress-strain properties are greatly affected as discussed below.

Under all conditions, the dimensions of the dispersed phase are restricted. Since the junctions between the endblocks and midblocks are located at the phase boundary, the domain thickness is limited to the distance which can be reached by the endblock segments extending into the domains from opposite sides. For commercial polymers, domain thicknesses have been both calculated and measured to be a few hundred angstrom or only a small fraction of the wavelength of visible light. If the domains are spheroidal, they do not scatter light. Thus, these thermoplastic rubbers are generally transparent, in spite of the large differences in refractive index between the two phases. With rodlike or lamellar morphologies, some light scattering and turbidity may exist.

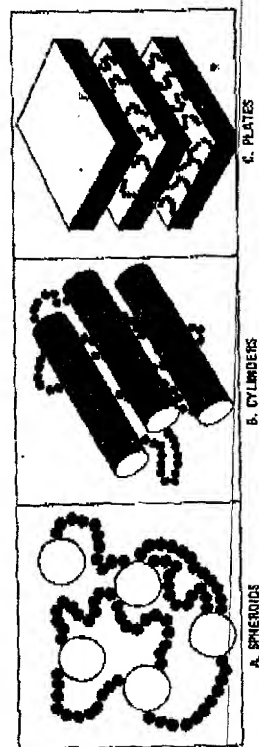


Fig. 11-3. Polystyrene domain configurations or morphologies.

Properties of Neat Thermoplastic Rubbers

Thermoplastic rubbers are sold commercially in the form of powder, crumb, porous pellets or dense pellets. Bulk densities range from about 240 kg/m^3 (15 lb/ft^3) for crumb to about 480 kg/m^3 (30 lb/ft^3) for pellets. Some thermoplastic rubbers are dusted with about 1% of a dusting agent, such as talc, to minimize the tendency to block on long-term storage under warm conditions. The specific gravity of a solvent cast or molded film of the thermoplastic rubber is about 0.92.

Hardness and tensile properties of the thermoplastic rubber depend on the styrene content and the type of rubber midblock in the polymer. The styrene content of thermoplastic rubbers used in pressure-sensitive adhesives is usually between about 15%w and 30%w. Hardness varies from about 35 Shore A for a 15%w styrene S-I-S polymer to about 75 Shore A for a 30%w styrene S-EB-S polymer. The stress/strain curves for these two polymers are shown in Fig. 11-4. Both polymers show stress/strain properties characteristic of vulcanized rubbers. However, the soft, 15%w styrene S-I-S polymer has a low 300% modulus, 0.7 MPa (100 psi), a moderate tensile strength, 20 MPa (3000 psi), and high elongation at break (1400%). The harder, 30%w styrene S-EB-S polymer has a much higher 300% modulus, 5.9 MPa (850 psi), a high tensile strength, 41 MPa (6000 psi), and much shorter elongation at break (600%). The hardness and tensile properties of other neat thermoplastic rubbers are generally intermediate between the extremes of the two polymers just described.

Solution viscosities of thermoplastic rubbers depend strongly on the solvent composition. This behavior will be discussed later in this chapter. However, in a solvent such as toluene, which dissolves both the polystyrene endblocks and the rubber midblock, solution viscosities are relatively low. The solution viscosity of a 25%w solution of most thermoplastic rubbers in toluene will be from about 1.0 to 10 Pa·s at 25°C.

Melt viscosities of neat thermoplastic rubbers can be extremely high at low shear rates. Typically, melt viscosities are 10^4 to 10^5 Pa·s at about 170°C and a 1 sec^{-1} shear rate. As will be discussed later in this chapter, melt viscosities at higher shear rates can be several orders of magnitude lower.

GENERAL FORMULATING PRINCIPLES

Phase Association of Ingredients and Morphology

As is the case with many conventional rubbers used in pressure-sensitive adhesives, such as natural rubber and SBR, thermoplastic rubbers have

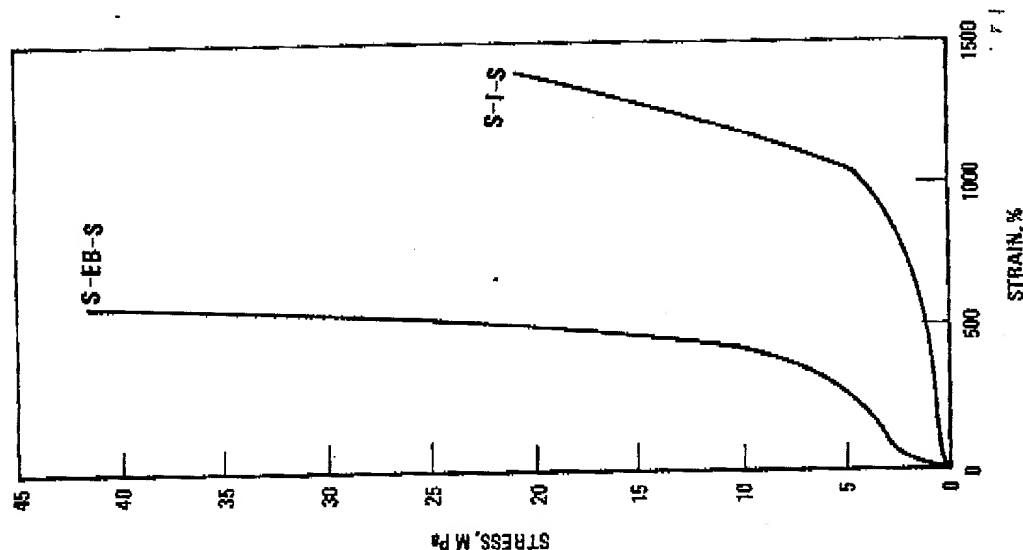


Fig. 11-4. Typical stress-strain curves for thermoplastic rubbers.

little inherent tack. Therefore, the rubber must be compounded with tackifying resin and, in some cases, with plasticizer to develop the required tack. However, since thermoplastic rubbers are two-phase systems, more care must be taken in formulation development with thermoplastic rubbers than

with conventional, single-phase homopolymer or random copolymer rubbers.

In homopolymers or random copolymers, additives have only one phase with which to interact. In thermoplastic rubbers, additives have two phases with which to interact. Thus, an equilibrium will be established among the additives, the rubber network and the polystyrene domains. Possible interactions include an association of the additive with the rubber phase, with the polystyrene domains, with both phases, or with neither phase (resulting in formation of an independent third phase).

A simple but qualitative test which can be used to determine with which phase of a thermoplastic rubber a given resin is compatible is the following. Cast thin films from toluene solutions of a 1:1 mixture of resin and crystal grade polystyrene and of a 1:1 mixture of resin and polyisoprene or polybutadiene. Clarity of the dried film indicates mutual solubility; turbidity indicates incompatibility and phase separation.

The importance of the knowledge of the compatibility of a resin with each phase of the thermoplastic rubber lies in the effect of an endblock compatible resin and a midblock compatible resin on the stiffness and stress-strain properties of the rubber. The stress-strain properties of a thermoplastic rubber formulation are closely related to the morphology of the endblock phase and the midblock phase which is related to the volume ratio of the two phases.

Effect of Phase Ratio. As the endblock concentration in an unfilled thermoplastic rubber increases, the shape of the stress-strain curves change as shown in Fig. 11-5. These particular curves apply to solution-cast films prepared from a series of experimental S-B-S polymers. The total molecular weight for each polymer was held constant; only the styrene content was varied.

At polystyrene endblock concentrations of 20-30%w, the stress-strain curve resembles that of a vulcanized rubber. At concentrations above and about 33%w, the phenomenon of "drawing," commonly exhibited by thermoplastics, appears. This occurs when a continuous rodlike or lamellar endblock network exists as suggested in Fig. 11-3. When such a sample is stretched, an initial yield stress is observed. Then, as the relatively weak plastic structure is disrupted by further elongation, drawing occurs. When the stress is released, the plastic network will gradually reform. Higher temperatures will speed reforming of the plastic network. At higher endblock concentrations, the plastic phase is continuous and the midblock phase dispersed to give a system resembling high impact polystyrene.

Effects of Additives. The ratio of endblock phase to midblock phase can be varied by adding materials which associate preferentially with one

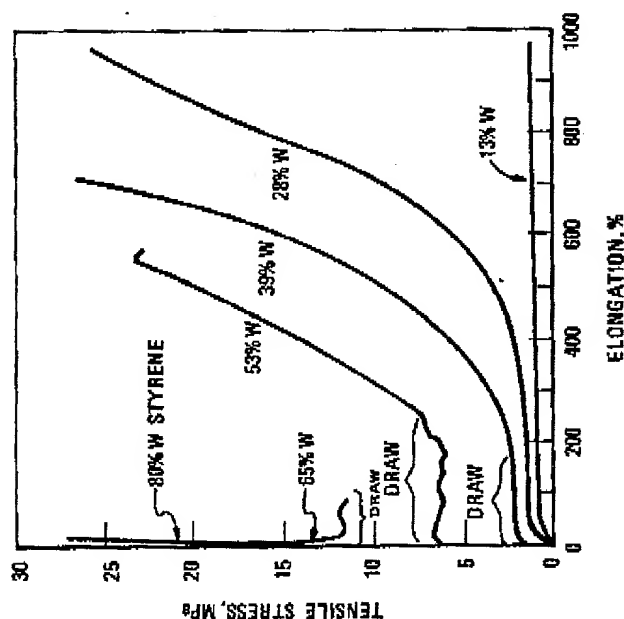


Fig. 11-5. Effects of polystyrene endblock concentration on linear S-B-S polymer tensile properties.

phase or the other. Coumarone-indene resins, for example, associate with the endblock phase in S-B-S and S-I-S polymers. Figure 11-6 shows how the initial portion of the stress-strain curve of the neat polymer (Curve B) is shifted (Curve A) when the endblock phase concentration is increased by adding an endblock resin. Curve C shows that the reverse occurs when a tackifying resin or a plasticizing oil which associates with the rubber phase is added to the neat polymer.

Effect of Solvent Blends. Because of the two-phase nature of thermoplastic rubbers, physical properties of films can be altered, in a third manner. Films cast from mixed solvent systems best demonstrate the principle; in general, the properties will be determined by the component of the solvent system which evaporates last.

Figure 11-7 shows stress-strain curves for films of an S-EB-S rubber cast from different solvents. Curve A is for a film cast from a 60/40%v blend of *n*-hexane/MEK. In this case, the last component to evaporate is MEK, which dissolves the polystyrene phase only. Thus, the rubber midblock phase precipitates first and the polystyrene phase last, so that a continuous polystyrene phase tends to be formed rather than discrete polystyrene do-

butyl acetate/Shell Sol 340EC. In this case, the last solvent to evaporate is Shell Sol 340EC, a very poor solvent for polystyrene, and the polystyrene is precipitated first, forming more discrete domains and fewer styrene continuous regions.

Properties intermediate to those shown by the three curves in Fig. 11-7 can be achieved by proper choice of solvents and solvent blends. Annealing the films represented by Curves A and C will tend to shift both curves toward the intermediate equilibrium position of Curve B. The rate at which the films anneal is temperature-dependent. Annealing effects may be encountered in processes where the film passes through a high-temperature drier.

Choice of Compounding Ingredients

Resin selection is probably the most important aspect in the development of pressure-sensitive adhesive formulations based on thermoplastic rubbers. When considering the effects of resins on adhesive properties, the distinction must be made between the effects of midblock compatible resins and the effects of endblock compatible resins, since their effect on tack is widely different.

Rubber Phase Associating Resins. Aliphatic olefin derived resins, rosin esters, polyterpenes, and terpene phenolic resins derived from petroleum or turpentine sources and having relatively low solubility parameters tend to associate with the rubber midblocks and not with the polystyrene endblocks. As the molecular weights or softening points of these resins are lowered, their solubility in the endblocks increases. A partial list of commercial resins in this category is presented in Table 11-1.

The primary function of a midblock compatible resin is to develop tack in the thermoplastic rubber. This type of resin can also serve to improve the specific adhesion of the midblock phase toward polar substrates, as processing aids for the midblock phase, and to alter the modulus of the adhesive. Addition of predominantly midblock-associating resins tends to soften the compound by decreasing the modulus and reduces the tendency to draw as discussed earlier. These latter effects occur as the addition of midblock resin increases the fraction of the midblock phase in the system, causing the morphology of the dispersed endblock phase to become more spheroidal (less continuous).

Midblock compatible resins in this category with glass transition temperatures greater than that of the rubber midblock phase will increase the glass transition temperature of the rubber-resin blend. This will result in reduction of low temperature tack and flexibility. Partial compensation for this reduction can be obtained through the selection of midblock plasti-

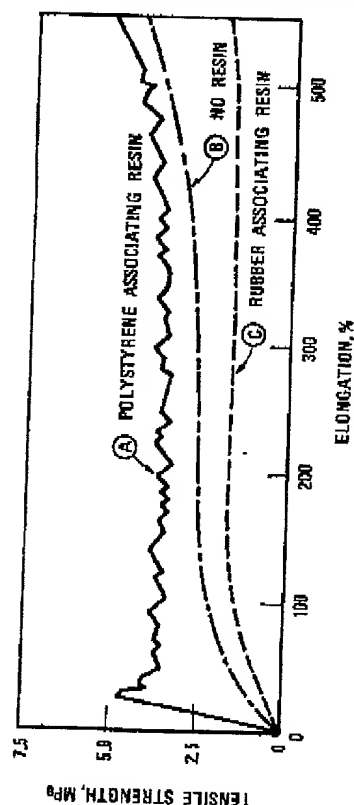


Fig. 11-6. Effect of polystyrene endblock and rubber midblock associating resins on tensile properties of thermoplastic rubber.

main. The curve shows an initial yield, followed by cold drawing, and a final rise in stress to break point.

Curve B shows the stress-strain behavior for the film cast from solution in toluene, a relatively good solvent for both phases. This curve represents a structure close to an equilibrium state because the solvent is a good solvent for both phases.

Curve C is for a film cast from a 16/20/64%v blend of ethylbenzene/*n*-

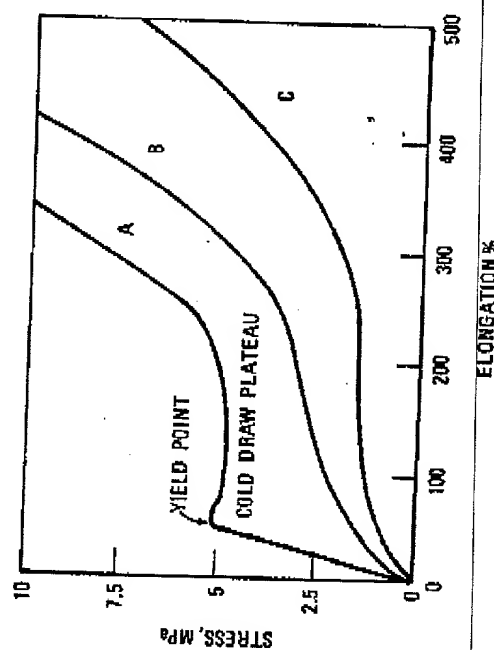


Fig. 11-7. Effect of solvent systems on physical properties of solution cast films of an S-EB-S polymer (Kraton® G 1650 rubber) at 23°C.

Table 11-1. Rubber phase associating resins for thermoplastic rubbers.

CHEMICAL TYPE	SOFTENING POINT (°C)	TRADE NAME	SUPPLIER
Polymerized mixed olefin	100,115,130	Eastman Resin	Eastman Chemical
Polymerized mixed olefin	100,120	Esorez 1300 series	Exxon Chemical
Polymerized mixed olefin	100	Hercolac 95	Hercules
Polymerized mixed olefin	85	Imprez T85	ICI America
Polymerized mixed olefin	80,130	Nevlac	Neville
Polymerized mixed olefin	100	Picopal HM-200	Hercules
Polymerized mixed olefin	100	Picopal 95 BHT	Hercules
Polymerized mixed olefin	85	Quintone N180	Nippon Zeon
Polymerized mixed olefin	100	Sta-Tac	Reichhold
Polymerized mixed olefin	100	Sta-Tac R	Reichhold
Polymerized mixed olefin	100	Super Novlac 99	Neville
Polymerized mixed olefin	80,100	Super Sta-Tac	Reichhold
Polymerized mixed olefin	Liquid*, 75,115	Wingstack series	Goodyear
Rosin Esters			
Glycerol ester of highly stabilized resin	82	Foral 85	Hercules
Pentaerythritol ester of highly stabilized resin	94	Foral 105	Hercules
Methyl ester of hydrogenated rosin	Liquid*	Hercolyn D	Hercules
Pentaerythritol ester of hydrogenated rosin	104	Pentolyn H	Hercules
Triethylene glycol ester of hydrogenated rosin	Liquid*	Staybelite Ester 3	Hercules
Glycerol ester of hydrogenated rosin	114	Staybelite Ester 10	Hercules
Polyterpenes and Derivatives			
Polyterpene	85,135	Piccolyte A	Hercules
Polyterpene	Liquid*	Piccolyte S10	Hercules
Polyterpene	85,115	Zonarez 7000 series	Arizona Chemical
Polyterpene	10,125	Zonarez B series	Arizona Chemical
Terpene phenolic	100	Piccolyn A-100	Hercules
Modified polyterpene	110	XPS 502	Hercules
Low Softening Point Endblock Resins			
Alkylaryl	Liquid*	Picovar AP10, AP25	Hercules
Hydrogenated Resins			
Saturated alicyclic hydrocarbon	85,125	Arkon P series	Arakawa
Hydrogenated mixed olefin	85,125	Esorez 5000 series	Exxon

* Because of their low molecular weight, these resins are soluble in both the endblock and midblock phases of thermoplastic rubbers.

cizers that have very low T_g 's. However, using low molecular weight plasticizer may also have an effect on the upper service temperature as the result of some unavoidable plasticizing of the endblocks. The importance and application of altering the T_g of thermoplastic rubber compositions is discussed more fully under low temperature labels and tapes in the latter part of this chapter.

Endblock Phase Associating Resins. Polyaromatics, coumarone-indene resins and other high solubility parameter resins derived from coal tar or petroleum and having softening points above about 85°C tend to associate with the polystyrene endblocks and not with the rubber midblocks. As the molecular weights or softening points of these resins are lowered, their solubility in the midblocks increases. A list of typical and commercial endblock associating resins is presented in Table 11-2.

Addition of nonplasticizing endblock-associating resins tends to stiffen the compound by increasing the modulus and increasing the tendency to draw as discussed previously. This occurs as the fraction of endblock phase increases and its morphology becomes more rodlike or lamellar. In pressure-sensitive adhesives, only a limited amount of high softening point endblock compatible resin can be included in the formulation, before the stiffness increases and the aggressive tack is reduced to unacceptable levels. Somewhat higher levels of endblock resin can be included if the adhesive also contains a plasticizer to offset the reduction in tack.

Higher softening point resins in this category may also tend to increase the glass transition temperature T_g of the endblock phase. This results in the

Table 11-2. Endblock phase-associating resins for thermoplastic rubbers.

CHEMICAL TYPE	SOFTENING POINT (°C)	TRADE NAME	SUPPLIER
Poly(phenylmethylstyrene)	100,115,145	Auroco 18 series	Amoco Chemical
Coumarone-indene	155	Cumar LX-509	Neville
Coumarone-indene	Liquid*	Cumar P-25	Neville
Coumarone-indene	100	Cumar R-16	Neville
Alkylated aromatic hydrocarbon	140	Newchem 140	Neville
Heat-reactive hydrocarbon	150	Nevdene LX-68.5-180	Neville
Polyalkylated aromatic polyindene	70,140	Pico 6000 series	Hercules
Polystyrene	100	Picodlastic D-150	Hercules
Poly(phenylmethylstyrene/vinyl toluene copolymer	100,120	Picocox	Hercules
Alkyl aromatic polyindene	Liquid*	Picovar AP10, AP25	Hercules
Alkyl aromatic polyindene	130	Picovar 130	Hercules

* Because of their low molecular weight, these resins are soluble in both the endblock and midblock phases of thermoplastic rubbers.

formulation retaining its cohesive strength at higher temperatures. Low softening point endblock resins have the reverse effect, namely, to lower the tensile strength at elevated temperatures, to cause the tack in heat-activated adhesives to develop at lower temperatures and to reduce the temperature at which the formulation can be handled as a hot melt.

Plasticizers. Plasticizers perform the following functions in adhesives based on thermoplastic rubbers: decrease hardness and modulus at room temperature, eliminate drawing, enhance pressure-sensitive tack, reduce melt and solution viscosity, decrease cohesive strength or increase plasticity if desired, and substantially lower raw material costs. The properties of a plasticized formulation are highly dependent upon the plasticizer composition, its solubility parameter, and its molecular weight.

It is usually true that the best plasticizer for use with thermoplastic rubbers in pressure-sensitive adhesives is one which is completely insoluble in the endblock phase, completely miscible with the midblock phase, and low in cost. Low volatility, low viscosity, low density, and resistance to degradation are also desirable characteristics. Various hydrocarbon oils whose average solubility parameters are below those of the midblocks, but not too far below, satisfy these requirements reasonably well.

Hydrocarbon oils are usually mixtures of molecular species which can be classed as aromatic, naphthenic, and paraffinic. When these oils are added to thermoplastic rubber, fractionation may occur with the aromatics concentrating in the endblock domains. Reduced cohesive strength at ambient and elevated temperatures typically results from using oils containing as little as 2-3% aromatics.

Typical hydrocarbon plasticizing oils and oligomers are listed in Table 11-3. They are arranged in order of increasing solubility parameter. Oils with the lowest solubility parameter and highest molecular weight are the least soluble in the endblock phase and will have the least effect on high temperature strength of thermoplastic rubber formulations. These same oils will also have the lowest solubility in the rubber phase and thus have the most tendency to bleed out when present in high concentrations.

Selection of a plasticizer involves balancing the various plasticizer characteristics to fit best any specific application. Plasticizers that are readily compatible with the polystyrene endblocks can solvate the endblock network and prevent the formation of strong physical crosslinks between the thermoplastic rubber molecules. Endblock domains will form as a separate phase, but instead of being hard and rigid at room temperature, they will be soft and fluid. Stress applied to this plasticized network will cause permanent deformation and flow. However, there may be instances in which plasticizing of the polystyrene domains is desirable, e.g., low cohesive

Table 11-3. Properties of plasticizing oils.

TRADE NAME	SUPPLIER	SOLUBILITY PARAMETER δ_p (HILDEBRANDS) ^a	AVERAGE MOLE WEIGHT ^b	SPECIFIC GRAVITY (15.6°C)	VOLATILITY LOSS (22 HR @ 107°C, WEIGHT %)	OIL ABSORBED BY AN S-B-S POLYMER ^c (PHR)
Polypropylene C-60	Armco Chem. Corp.	6.55	800	0.86	0.1	25
Polybutylene-18	Chevron Chem. Co.	6.95	600	0.88	0.1	39
Tufflo 6206	Atlantic Richfield Co.	7.06	660	0.88	0.05	31
Polybutylene-12	Chevron Chem. Co.	(7.04)	530	0.88	—	(53)
Tufflo 6056	Atlantic Richfield Co.	7.18	550	0.87	0.3	56
Polybutylene-8	Chevron Chem. Co.	(7.18)	440	0.86	—	(75)
Kaydol	Witco Chem.	7.34	480	0.89	—	82
Tufflo 6026	Atlantic Richfield Co.	7.29	410	0.86	1.0	76
Polybutylene-6	Chevron Chem. Co.	7.34	315	0.84	10	103
Tufflo 6016	Atlantic Richfield Co.	7.51	390	0.85	2.0	106
Tufflo 6204	Atlantic Richfield Co.	7.60	440	0.92	0.5	96
Shellflex 371	Shell Chem. Co.	7.60	410	0.90	0.9	112
Tufflo 6094	Atlantic Richfield Co.	7.60	410	0.92	0.8	95
Tufflo 6054	Atlantic Richfield Co.	(7.66)	380	0.92	1.3	(127)
Tufflo 6014	Atlantic Richfield Co.	7.73	320	0.89	12.0	214

^a Calculated from experimentally determined surface tension, average mole weight, and specific gravity. Values in parentheses were interpolated.

^b By bulboscopic methods of Mechrolab osmometer.

^c Grams of oil absorbed by 508 to 1000 mm film of Kraton D-1101 rubber at room temperature per 100 g original weight after soaking 100 hr. Films were prepared by casting from toluene solution on mercury and drying very slowly. Parenthetical values were interpolated or extrapolated from related data.

fillers increase the stiffness and reduce aggressive tack, although tack reduction may be useful in certain applications. Carbon black, which functions as a pigment and screening ultraviolet stabilizer, forms permanent gel structures with the unsaturated midblocks. This reduces solubility and thermoplasticity.

Stabilizers. Unsaturated thermoplastic rubbers are susceptible to attack by oxygen, ozone, and UV radiation, especially when stressed. Therefore, stabilizers should be incorporated in the formulation to provide resistance to attack during processing and to protect the finished adhesive during its service life.

Although the stability of the saturated thermoplastic polymers is substantially better, it is good practice to include stabilizer in formulated products containing these more stable polymers.

In choosing a stabilizer package, it should be noted that the rubber midblock is more susceptible to attack than the polystyrene domains. It is, therefore, more advantageous to use stabilizers which associate primarily with the rubber midblock and protect double bonds along the midblock chain.

The two types of rubber midblock—polybutadiene and polyisoprene—in the unsaturated thermoplastic rubbers behave differently when attacked by oxygen, ozone, or UV radiation. S-B-S polymers tend to crosslink, with films becoming hard and brittle. S-I-S polymers tend to undergo chain scission, whereby films become softer and tackier.

Protection against oxygen attack. Oxidative attack occurs in two ways. One is under normal end-use conditions; the other occurs at high temperature under shear. The latter instance would be typical during the mixing of hot melts, especially if the operation takes place in air over an extended period.

A list of some antioxidants found to be effective in thermoplastic rubber formulations is given in Table 11-4. Their relative physical effectiveness will vary with aging conditions (temperature, amount of contact with air) and with the criteria used to judge the amount of degradation. Combinations of antioxidants may be more effective than one alone.

Protection against ozone attack. Unsaturated thermoplastic rubbers are susceptible to degradation by ozone, particularly when under stress. Degradation is evidenced by surface crazing and hardening.

Table 11-5 lists some antioxidants for use in thermoplastic rubber formulations. Antioxidants such as nickel dibutyl dithiocarbamate (NBC) and Penzone B improve the resistance of thermoplastic rubbers to ozone.

strength pressure-sensitive adhesives. This can be affected by choosing endblock plasticizing resins.

An example of an endblock plasticizer which destroys cohesive strength is dioctylphthalate (DOP), commonly used in plasticized polyvinyl chloride (PVC) compositions. Adhesives based on a thermoplastic rubber with polystyrene endblocks should be carefully tested when intended for direct contact with PVC highly plasticized with low molecular weight phthalate esters, which can diffuse into the endblock phase and destroy the cohesive strength. The most effective way to prevent the loss of cohesive strength in a situation of this type is to replace the DOP with a nonmigrating plasticizer, such as an intermediate or medium high molecular weight polymeric plasticizer (e.g., Paraplex G-50 or G-54 from Rohm and Haas Company). Another way is to use a primer or barrier coating which restricts the tendency for plasticizer migration into the adhesive mass.

Other Polymers. Low concentrations of thermoplastic rubber substituted into adhesives based on conventional unvulcanized rubber like natural rubber, polyisoprene, and SBR will upgrade cohesive strength, will lower solution viscosity, and may improve adhesive strength. Conversely, use of a limited amount of a conventional rubber in a thermoplastic rubber formulation may increase solution or melt viscosity and lower costs with limited loss in cohesive strength or other properties when these goals are desirable.

The degree of compatibility between other polymers must be considered in formulating adhesives. S-I-S polymers are essentially miscible with polyisoprene and natural rubber. S-B-S polymers mix well with SBR and polybutadiene rubbers. In other combinations, however, turbidity of cast films, slow phase separation in solution, and other evidence of molecular incompatibility may appear. Nevertheless, rubbers of the incompatible type, including neoprene and nitrile rubbers, may form commercially useful mixtures if mixing problems, tendency to phase separate, turbidity, etc., are appropriately handled. Methods of offsetting incompatibility include the use of high shear mixing, formulating for high solution viscosities, mixing immediately before use, and inclusion of compatibilizing resins in the formulation.

Blending thermoplastic rubber into ethylene-vinyl acetate (EVA) polymers with low to medium vinyl acetate content is roughly equivalent to increasing the vinyl acetate content of the EVA polymer. The mixtures become softer and exhibit better flexibility at ambient and low temperatures.

Fillers. Nonreinforcing fillers such as clay, talc, whiting, etc., can be used in pressure-sensitive adhesives to pigment the adhesive and to lower raw material costs. The amount of filler which can be used is limited because

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Table 11-5. Antiozonants for thermoplastic rubbers.

CHEMICAL COMPOSITION	TRADE NAME	SUPPLIER
Nickel dibutyl diithiocarbamate	NBC	DuPont
Dibutyl thiourea	Pennzone B	Pennwalt
Undisclosed	Ozone Protector 80	Reichhold

but also produce discoloration and staining. Improvement is also provided by Ozone Protector 80, a nonstaining antiozonant, but considerably higher loadings are required than with NBC or Pennzone B. It should be noted that Pennzone B is not suitable for hot melt formulations, as it accelerates the crosslinking of the rubber segments.

Protection against ultraviolet radiation. Degradation by exposure to UV light is denoted by discoloration and embrittlement or strength loss of thermoplastic rubber compounds. In the vast majority of indoor applications, this type of degradation is not a consideration. If, however, direct exposure to sunlight is expected, unsaturated thermoplastic rubbers will be susceptible and must be protected, particularly with clear, nonpigmented formulations. In addition, care should be used to select stable resins and plasticizers in formulating UV resistant pressure-sensitive formulations.

Table 11-6 lists a variety of UV light inhibitors for use with thermoplastic rubbers. One or more of these stabilizers should be added during compounding, at the level of about 0.5 phr. With opaque products, even

Table 11-6. Ultraviolet inhibitors for thermoplastic rubbers.

CHEMICAL COMPOSITION	TRADE NAME	SUPPLIER
2,4-dihydroxybenzophenone	Uvarel 400	GAF Corp.
Substituted hydroxyphenyl benzotriazole	Tinuvin 326	Ciba-Geigy Co.
Substituted benzotriazole	Tinuvin P	Ciba-Geigy Co.
2-Hydroxy-4-(2-hydroxy-3-methacryloyloxy)propylbenzophenone	Permaseorb MA	National Starch and Chemical Corp.
Octylphenyl salicylate	Eastman OPS	Eastman Chemical
Resorcinol monobenzoate	Eastman RMB	Eastman Chemical
1,3,5-Trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl) benzene	Antioxidant 330	Ethyl Corp.
Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate	Irganox 1076	Ciba-Geigy Co.
Tetrakis methylene 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate methane	Irganox 1010	Ciba-Geigy Co.

Table 11-4. Antioxidants for thermoplastic rubbers.

CHEMICAL COMPOSITION	TRADE NAME	SUPPLIER	STARTING LEVEL (phr)
Zinc dibutyl diithiocarbamate	Butyl Zimate	R. T. Vanderbilt Co.	1-5
	Butyl Ziram	Pennwalt Co.	0.3-1
	Irganox 1010	Ciba-Geigy Co.	0.5-2
Tetrakis methylene 3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate methane	Plastinox 2246 ^a	American Cyanamid Co.	0.3-1
2,2-Methylenebis(4-methyl-6-tert-butyl-phenol)	Antioxidant 330	Ethyl Corp.	0.3-1
1,3,5-Trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl) benzene	Irganox 565	Ciba-Geigy Co.	0.5-1
2-(4-Hydroxy-3,5-tert-butyl anilino) 4,6-bis(m-octyl thio)-1,3,5-triazine	Plastinox 425 ^a	American Cyanamid Co.	0.5-1
2,2-Methylenebis(4-ethyl-6-tert-butyl phenol)	Santowhitc crystals	Monsanto Chemical Co.	1-2
4,4'-Thiodis(6-tert-butyl-m-cresol)	Polygard ^a	Unifoyal Chem. Co.	3-5
Tris(honylated phenyl) phosphite			

^a May produce colored formulations.^a Polygard may be useful at high temperatures (150 to 200°C) at the high levels shown.

concentrations and their interaction with each other, finding the proper combination for a particular adhesive can be a large task. In this section, the use of adhesive property contour diagrams is suggested as a rapid and reliable approach to formulation development.

An adhesive property contour diagram can be thought of as a topographic map. The X and Y axes of the map are the concentrations of two of the compounding ingredients. The lines on this rectangular concentration grid are contours at which the particular adhesive property has a constant value. Thus, at any point on the grid representing a particular combination of the two ingredients, the value of the adhesive property is immediately known.

The construction and use of adhesive property contour diagrams can be illustrated by the following practical example on the development of a formulation for a hot melt pressure-sensitive adhesive for a general-purpose masking tape.

To begin, the adhesive formulator must select the critical property requirements which must be met. In this example, the adhesive must have a low value for rolling ball tack, moderate holding power to kraft paper, and low melt viscosity. Using the formulating principles presented, the formulator must then select the two ingredients most likely to affect these critical properties. In this example, the properties will be dominated by the concentration of midblock resin and midblock plasticizer. Adhesives are then prepared at compositions corresponding to selected points on the concentration grid covering the range of interest. In this example, sixteen adhesives were initially prepared containing Kraton D-1107 rubber, midblock resin (Winglack 95) at 75, 100, 150, and 200 phr, each containing 0, 25, 50, and 100 phr of midblock plasticizer (Shellflex 371). The performance of these adhesives in the critical property tests is then determined and the results are written at the appropriate point on the concentration grid. From these data, contour lines are drawn through points at which it is estimated that the adhesive property will have a constant value. If necessary, regions of special interest may be further refined by preparing and testing more samples in the area.

There are many advantages of developing adhesive formulations using contour diagrams. One major advantage is that they clearly show how properties change with changes in the concentration of ingredients. The contour diagram of rolling ball tack in Figure 11-8 clearly shows that with increasing plasticizer content, higher loadings of tackifying resins can be tolerated without loss of tack. The contour diagram of holding power clearly shows the very detrimental effect of increasing plasticizer concentration on holding power.

Another advantage of contour diagrams is that by superimposing contour diagrams of the critical properties, the allowable concentration range

without UV stabilizers, the addition of up to five parts of a reflective filler like TiO_2 or a light-absorbing filler like carbon black will afford excellent protection.

Basic Formulating Principles

The characteristics of formulations based on thermoplastic rubber depend on the various compounding ingredients chosen, the interaction of these ingredients with the two polymer phases present, and the concentration chosen. The following generalizations, although they may not be valid for all compositions, provide useful guidelines for formulation development studies.

1. Endblock resins will raise or lower the upper service temperature limit, depending on their softening point. Midblock resins will also increase or decrease service temperature limit depending on their softening point.
2. Midblock resins and plasticizers lower the room temperature modulus and soften adhesive formulations. Endblock resins tend to raise the modulus by increasing the percentage of hard endblock phase.
3. Pressure-sensitive tack tends to be favored by polyisoprene midblocks over polybutadiene midblocks; such tack is produced by some midblock resins and not by others. All solid endblock resins tend to lower pressure-sensitive tack by increasing modulus; rubber phase plasticizers tend to increase aggressive tack by lowering modulus.
4. Peel strengths tend to increase with increasing formulation modulus; specific adhesion to polar or metal substrates tends to be increased by polar, unsaturated, or aromatic resins and to be decreased by hydrocarbon plasticizers.
5. Melt and solution viscosities tend to be markedly decreased by both resins and plasticizers; inorganic fillers will tend to increase viscosity.

Other guiding principles can be established by experience and by considering a given application in the light of background information already presented in this chapter and specific examples of tape and label formulations discussed at its conclusion.

Basic Formulation Development Technique

A final formulation developed for a specific end-use will contain some combination of the various ingredients just discussed. Since adhesive properties depend not only on the types of ingredients but also on their

must be controlled during manufacturing to ensure satisfactory product performance.

Contour diagrams can be constructed using data obtained on samples cast from solutions, even if the intended use of the adhesive is for hot melts. Adhesive properties will depend upon the characteristics of the solvent from which the adhesive was cast. However, if the solvent used in preparing the adhesive is a good solvent for all ingredients in the formulation, the measured properties will be very similar to properties of the same adhesive prepared as a hot melt, assuming the hot melt has not been degraded. Reagent-grade toluene is usually a satisfactory solvent. There are two advantages of doing the formulation development in solvent rather than in hot melt. First, the manpower required to mix the adhesive and prepare test samples is substantially less and thus the time required to develop contour diagrams will be less. Second, heat history or degradation of the adhesive during processing, a very important variable which can significantly affect adhesive properties, is eliminated. Data from the contour diagrams generated from the solution cast adhesives indicate the most appropriate combination of ingredients for use in the hot melt adhesive. However, if the hot melt adhesive does not have exactly the required properties, the contour diagrams also show trends which indicate how to adjust the concentration of the ingredients of the hot melt adhesive to reach the target performance properties.

APPLICATION OF FORMULATING PRINCIPLES

Understanding of the thermoplastic rubber molecule architecture, neat polymer properties, and general formulating principles forms the basis for making useful and competitive pressure-sensitive adhesive finished products.

Three general areas for consideration are identified:

1. pressure-sensitive adhesive product performance
2. adhesive manufacture
3. adhesive product manufacture (finished tape or label)

Guidance for the use of thermoplastic rubbers in solvent or hot melt pressure-sensitive adhesive systems is discussed in these categories in the following sections.

Adhesive Product Performance

How do we attack the finished adhesive product performance issue and select the right thermoplastic rubber polymer and formulation to do the

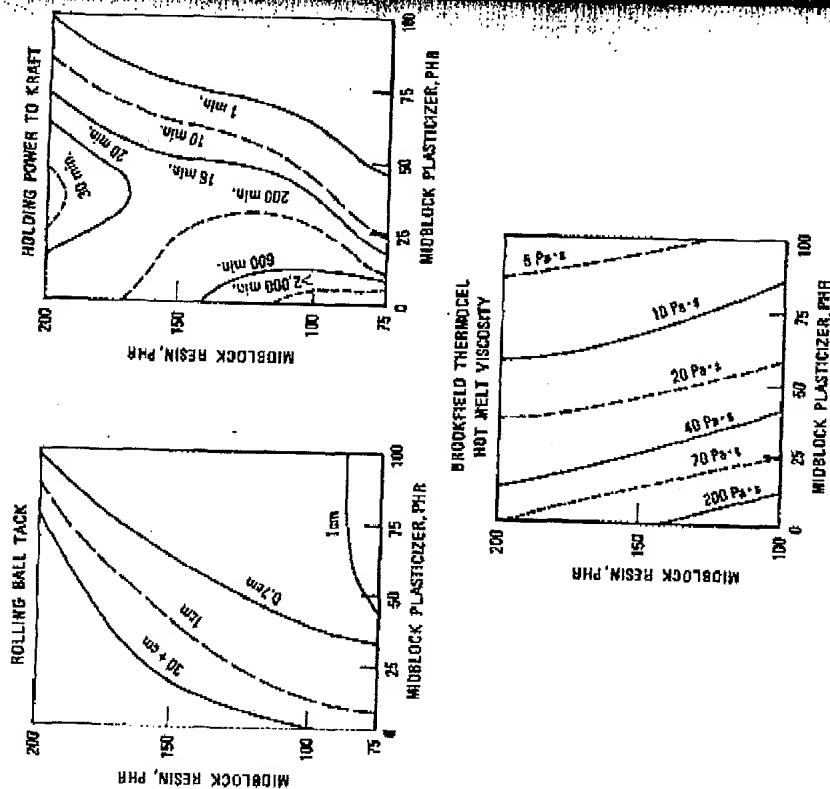


Fig. 1A-8. Effect of midblock resin and midblock plasticizer concentration on adhesive properties: contour isopleths for tack, holding power, and hot melt viscosity.

in which satisfactory performance can be obtained is immediately apparent. If there is no region of overlap in which all critical properties are met, it is immediately apparent that it is impossible to reach the required performance with these particular ingredients. If the requirements of the general-purpose masking tape adhesive used in this example were that rolling ball tack must be 1 cm or less, holding power must be at 200 min and melt viscosity must be less than $40 \text{ Pa} \cdot \text{s}$, superposition of the contour diagrams shows that the only practical formulation will contain about 125 phr of midblock resin and 25 phr of midblock plasticizer. The contour diagrams also show how sensitive the properties are to changes in concentration of the ingredients and thus how closely ingredient concentrations

job? The answer is by first defining the required performance, be it a new adhesive application with thermoplastic rubber, or an established adhesive product where thermoplastic rubbers are being considered.

Each approach to answering the performance question has its traps and pitfalls, centered on one basic assumption: test methods and results measure the desired performance because a correlation exists between methods/ results and actual performance. Decisions are made in judging formulations and adhesive quality on the assumption that this correlation is true. With materials that have a proven performance history in the field, it is a good assumption. For a different polymer or adhesive, the assumption may be faulty.

For example, superposition of temperature-time relationships to compare aging of different materials via measuring change in some property is a common tool (an Arrhenius plot). However, to make valid plots and comparisons, changes of state, e.g., glass transitions, crystalline melting points, must be considered in making tests and extrapolating results. For this reason, aging tests above the upper glass transition temperature T_g of block copolymers (T_g of styrene endblock about 92°C) are not valid indicators of block copolymer adhesive performance at lower temperatures for extended periods of time. Other polymers, natural rubber and acrylics for example, will not exhibit an elevated temperature T_g , and elevated temperature aging tests may be reasonable indications of long-term properties retention at lower temperatures. Care must be taken in generating and comparing such data.

These concerns suggest that past experience with familiar and established materials and the specifications established and existing for the materials and expected results in testing via standard methods are simply indicators of performance and not absolutes.

The following questions are relevant in this regard:

1. Are the test methods and criteria currently used in the familiar product related to the end-use performance?
2. What is the basis of the correlation between the test method and criteria which is established and the end-use performance?
3. Are the performance qualification test methods and criteria and the boundary range established for acceptable performance based on end-use performance need, or a property which characterizes the adhesive polymer type or its variability rather than finished product performance?
4. What other real performance characteristics of the established product or adhesive polymer are not defined or measured in the specifications or its tests, yet are known to be important in this product?

5. What new test method, criteria and guidelines should be established for a thermoplastic rubber adhesive which are relevant to the end-use performance, and will allow assessment of its performance on a sound basis? Is there a correlation with performance?

6. What structural differences between the current adhesive polymer and the block copolymer candidate may significantly alter results via the test method employed? Where can the structural differences in block copolymers be used to advantage?

7. What technical data need to be developed in order to verify performance via new test methods which reflect actual performance?

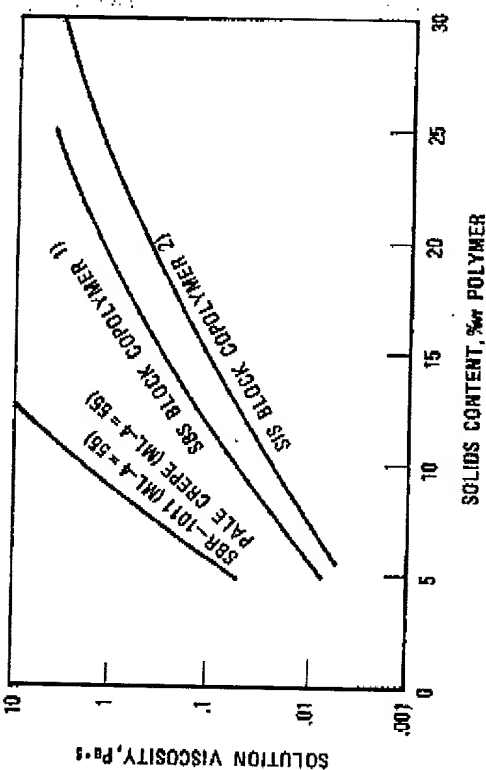
With any new or alternative adhesive system product, answers to these questions form a sound technical basis for judging the finished product, assuring quality in manufacture and developing product information which allows its introduction and successful use in the marketplace.

Adhesive Manufacture

Adhesive formulations are most frequently prepared from crumb or pelletized thermoplastic rubber by solvent solution or hot melt mixing techniques. Commercial thermoplastic rubbers are not offered as emulsions.

Thermoplastic rubbers have two distinct characteristics that differentiate them as a group from conventional rubbers, and that are important in considering adhesive manufacturing via solvent or hot melt mixing techniques.

Styrene endblock type thermoplastic rubbers produce low solution viscosities in a good polystyrene solvent, e.g., toluene. Thermoplastic rubbers without premodification have lower solution viscosities at comparable concentrations than do elastomers such as SBR, natural rubber and polychloroprene after milling. This is because thermoplastic rubbers have relatively low, precisely controlled molecular weights. Molecular weights are allowed to be relatively low because the ABA structure and polystyrene endblock domain network afford high cohesive strength at these comparatively lower molecular weights. Unvulcanized conventional rubbers rely primarily on chain entanglements for strength, thus molecular weights must be high, resulting in higher solution viscosities. Premastication (milling) of natural rubber is beneficial to producing lower solution viscosity, but this is energy-intensive. The adhesive system will require vulcanization or expensive accelerators to regain initial strength levels through crosslinking. Thermoplastic rubbers reform the polystyrene endblock network with simple solvent evaporation, and form the high strength structure without curing or accelerators. Thus, higher solids solutions at given viscosity, i.e., less solvent



- 1) KRATON® D 1101 RUBBER
2) KRATON® D 1107 RUBBER

Fig. 11-9. Viscosity of toluene solutions at 25°C for various rubbers.

required initially or to be recovered, are possible with thermoplastic rubbers when compared with conventional rubbers.

Solution viscosity is shown in Fig. 11-9 for linear S-B-S and S-I-S thermoplastic rubbers at various concentrations in toluene, along with viscosity for natural rubber and SBR. These data illustrate the lower viscosity obtainable with thermoplastic rubber than with NR and SBR, even after those materials have been milled to reduce their molecular weight.

Thermoplastic rubber compositions are melt processible. For the same molecular structure reasons, thermoplastic rubber compositions are easily melt processible, while conventional rubber compositions are not. At hot melt mixing temperatures, the polystyrene endblock domain structure is made fluid with heat and shearing. The system viscosity is low because block copolymer molecular weights are relatively low and the system endblock structure is fluid. Conventional rubbers of much higher molecular weight produce very high hot melt viscosities.

The following sections serve as a guide to preparing solvent solution adhesives and hot melt adhesives with thermoplastic rubbers in greater detail.

Solvent Behavior of Thermoplastic Rubbers. The behavior of thermoplastic rubber toward solvents is unique because it is comprised of

two different polymeric chains present in every molecule. Each midblock and endblock portion of the molecule has a characteristic solubility parameter.* Thus, the ability of the neat thermoplastic rubber molecule to be solvated is a strong function of the solvent or solvent blend chosen. Solvation viscosities can be varied over a wide range as a function of solvent choice or blend at a given solids level concentration. This characteristic can be used advantageously in developing formulations where adhesive solids level and viscosity must be closely balanced, or optimized, for given solvent coating equipment, as well as a means to alter drying rate characteristics.

In addition, a judicious choice of resins and resin concentrations can lead to enhanced solution viscosities, and potentially higher solids systems with less costly or more environmentally acceptable solvent blends.

For ABA thermoplastic rubbers, two solubility parameters are involved, one for the polystyrene endblock and one for the rubber midblock. A good solvent for a thermoplastic rubber must therefore be one which dissolves both endblock domains and midblock segments.

To illustrate, Fig. 11-10A indicates the approximate range of solubility parameter of solvents for rubber midblocks. The boundaries are not sharp near the extremes because the polymer molecules tend to collapse while still solvated. Figure 11-10B indicates, in a similar way, the range of solubility parameters of solvents for polystyrene endblocks. Figure 11-10C shows what happens when both blocks are combined in a single block copolymer molecule. A central range of solvents readily dissolves both blocks and gives low viscosity solutions. With solvents at the lower solubility parameter end, the polystyrene endblocks tend to remain associated and form what might be termed solvated endblock domains. In this region, solution viscosity increases rapidly with decreasing solubility parameter until rigid crosslinked-like gels are formed. With solvents at the high solubility parameter end, the situation is somewhat different. First, the midblocks become less and less soluble and tend to associate together while the endblocks are highly solvated. Opalescent solutions with time-dependent vis-

* Hildebrand's solubility parameter (represented by δ) is a measure of the total forces holding the molecules of a solid or a liquid together. It has the units of $(\text{cal}/\text{cm}^3)^{1/2}$. Every compound is characterized by a specific value of solubility parameter, although this value may not always be recorded in convenient literature references. Materials having the same solubility parameter tend to form homogeneous mixtures or to be miscible. Those with different solubility parameters tend to form separate layers or to be mutually insoluble. Other indexes of solvent compatibility (Kauri-Butanol value, aniline point, dilution ratio, etc.) can often be correlated with solubility parameter. For example, Kauri-Butanol values in the range of 20 to 100 for hydrocarbon solvents can be used to predict thermoplastic rubber solubilities. A solvent can be judged good or poor by comparison of its K-B value with those of known-good-or-poor solvents. (Discussions of solubility parameter concepts are presented in References (5) and (6). K-B values and solubility parameters for a range of commercial solvents are listed in Reference (7).)

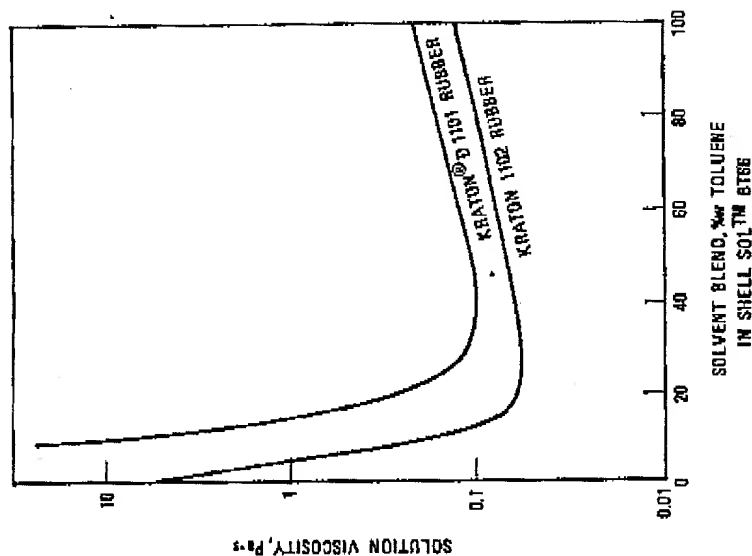
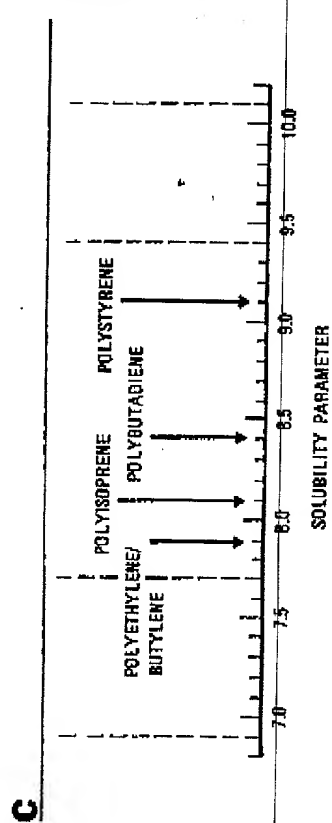
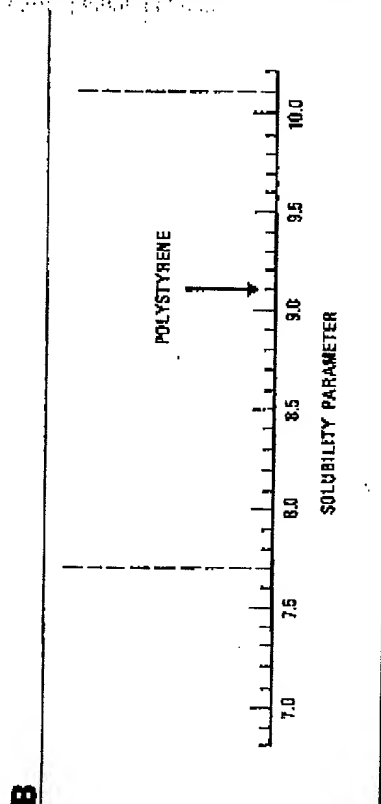
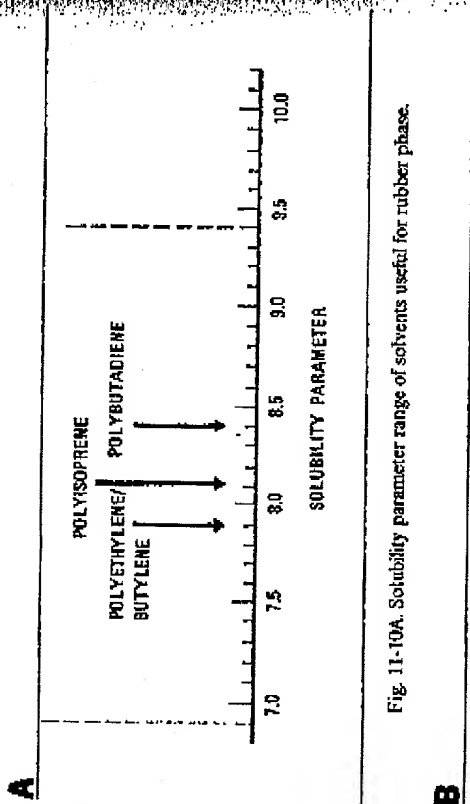


Fig. 11-11. Effect of toluene concentration on the solution viscosity of 15%W S-B-S thermoplastic rubbers in aliphatic hydrocarbon/toluene blends at 23°C.

cosities are formed. Thermoplastic rubber crumb can be dispersed in this sort of borderline solvent (for example, methyl ethyl ketone).

An example of these principles is shown in Fig. 11-11. These curves represent the viscosities of 15%w solutions of S-B-S thermoplastic rubbers in *n*-hexane/toluene solvent blends over a 0 to 100% toluene concentration solvent blend range. When an aliphatic solvent, such as *n*-hexane, or other pure solvents with solubility parameters below 7.4 are chosen, the S-B-S solution viscosity is much higher than that shown for a pure toluene solution of the same polymer. This is because *n*-hexane is a nonsolvent for the polystyrene endblock, while toluene dissolves both the midblock and endblock segments of the thermoplastic rubber molecule.

Increasing the toluene concentration in the blend or addition of other higher solubility parameter solvents, brings the polystyrene endblocks into

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solution, resulting in solvent blend solutions of lowered viscosity. Indeed, a minimum viscosity is shown in the 20-30%w toluene blend range for these polymers at a 15%w polymer concentration.

The solution viscosity is also dependent upon the molecular weight and a number of polystyrene arms in the thermoplastic rubber polymer, as well as actual weight percent polystyrene in the thermoplastic rubber polymer. These effects are shown for the two different linear S-B-S thermoplastic rubbers as shown in this same figure. While these curves are specific to these S-B-S polymers, similar behavior can be expected for S-I-S and S-EB-S thermoplastic rubbers in blended and pure solvents.

In the selection of a solvent system for a finished pressure-sensitive adhesive, one must consider all other components which are used in the thermoplastic rubber formulation. Resins and plasticizing oils are usually the most important in this regard.

Figure 11-12 demonstrates an interesting finding for the effect that addition of 100 phr of a tackifying resin (a rosin ester) has on solution

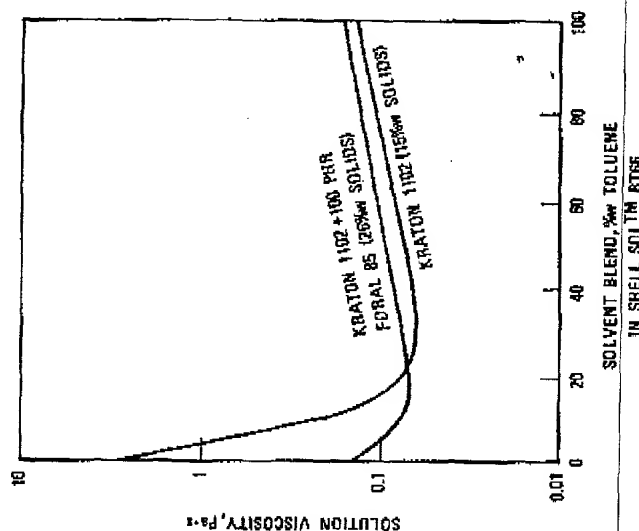


Fig. 11-12. Effect of a rosin-ester resin on the solution viscosity of an S-B-S thermoplastic rubber in aliphatic hydrocarbon/toluene blends at 23°C.

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viscosity in solvent blends of *n*-hexane and toluene for 15%w solids S-B-S solution (plot similar to Fig. 11-11). The net effect is that the addition of this resin has shifted the minimum solution viscosity position of the rubber-resin blend to a point where the concentration of a good endblock solvent, toluene, is lowered when compared to the neat polymer thermoplastic rubber solution minimum viscosity point. This suggests that the solution viscosity as a function of solvent blend can be perturbed by the addition of resins which can act to alter the net solubility parameter of the solvent system and shift the minimum viscosity position. In this case, the resin is acting more like toluene solvent in the rubber-resin solution, allowing a lower concentration of this good endblock solvent to achieve a minimum viscosity.

Contours of such interactions could be plotted for various resin types, resin concentrations, solids levels, and polymer types in order to map and optimize solution viscosities and solvent blends.

Table 11-7A shows results for a series of solution viscosity measurements made on S-I-S linear thermoplastic rubbers when blended with midblock and endblock resins at a constant solids level (60%) in toluene solvent. Table 11-7B shows the composition of these blends.

Comparing samples 1 and 2 or 6 and 7, the expected change in viscosity

Table 11-7A. Solution viscosity vs. resin level and type: constant 60%w compositions in toluene.

COMPOSITION NUMBER ^a	RESIN BLEND	RATIO OF S-I-S POLYMER ^{b,c} TO RESIN BLEND		SOLUTION VISCOSITY (Pa-s)
		1:1	5:7	
1 ^a	100% midblock	1:1	5:7	21.8
2 ^a	100% midblock	5:7	5:7	11.4
3 ^a	6:1 (midblock: endblock)	5:7	5:7	14.6
4 ^a	5:2 (midblock: endblock)	5:7	5:7	20.0
5 ^a	5:2 (midblock: plasticizing endblock)	5:7	5:7	9.2
6 ^a	100% midblock	1:1	5:7	110.0
7 ^a	100% midblock	5:7	5:7	33.4
8 ^a	6:1 (midblock: endblock)	5:7	5:7	47.5
9 ^a	5:2 (midblock: endblock)	5:7	5:7	88.4
10 ^a	5:2 (midblock: plasticizing endblock)	5:7	5:7	10.9

^a See Table 11-7B for detailed composition of solutions.

^b Sample Nos. 1-5 based on Kraton D-1107 rubber.

^c Sample Nos. 6-10 based on Kraton D-1111 Rubber.

Alternately, constructing a horizontal line at 50 weight percent solids, we find that a greater ratio of toluene to Shellsol B is necessary to achieve this solids level at 50 Pa-s viscosity with the formulation containing no additional endblock plasticizing resin (formulation A). In cases where aliphatic solvents are less costly than aromatics or more environmentally acceptable, utilization of formulation B over formulation A may be advantageous.

INGREDIENTS	SAMPLE	NO.
KRATON	D-1107	RUBBER
ESCOREZ	LX-509	RUBBER
CUMAR	AP-25	
PICCOVAR	371	
SHELLPLEX	1010	
IRGANOX		
		TOLUENE

INGREDIENTS	SAMPLE NO.	NO.
KRATON	D-1107	100
KRATON	D-1111	100
RUBBER		100
ESCOREZ	1310	100
CUMAR	LX-509	40
PIGCOVAR	AP-25	10
SHELLPLEX	371	1
IRGANOX	1010	1
TOLUENE		167.3

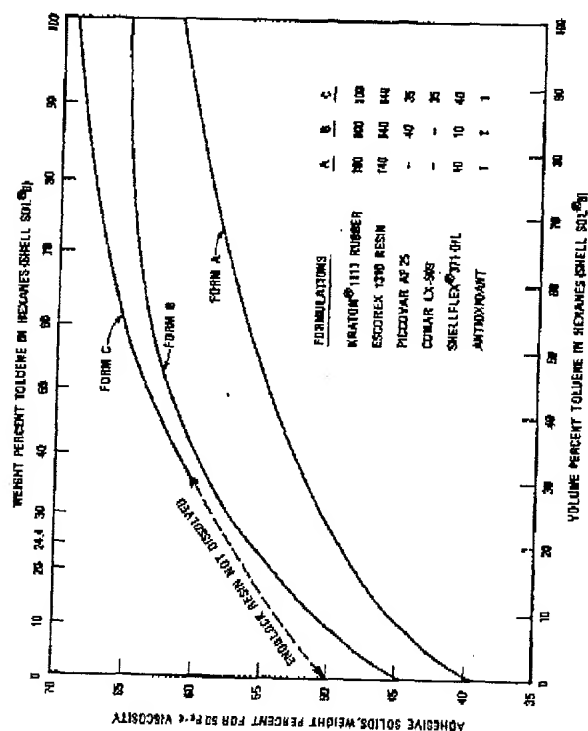


Fig. 11-13. Effect of toluene concentration on pressure-sensitive adhesive solids and composition in solvent blends to produce constant 50 Pa · s solution viscosities.

The plot for formulation C is simply shown to indicate that the high softening point, highly associative endblock resin used (Cumar LX-505) requires a given level of aromatic solvent in the solvent blend before it will dissolve in this system, about 30%. Further, formulation C is the most dilute polymer of the three, and shows the highest achievable solids at any given aliphatic-aromatic solvent blend ratio at a 50 Pa's viscosity.

Drying times are affected by variations in the solids level of a formulation and by the choice of a solvent, or solvent blend. In this aspect of solution processing, the advantage lies with the less ideal solvents. That is, solvent release is faster with poor solvents than with good solvents because the last traces of poor solvent are not as tightly held by the thermoplastic rubber molecule.

Solvent effect on drying time is shown in Fig. 11-14 for toluene and a blend of toluene with a typical aliphatic solvent of low boiling point and low solubility parameter (approximately 7.3). The illustration shows that the use of the aliphatic solvent greatly reduces evaporation time, due to its greater volatility and lower solubility parameter.

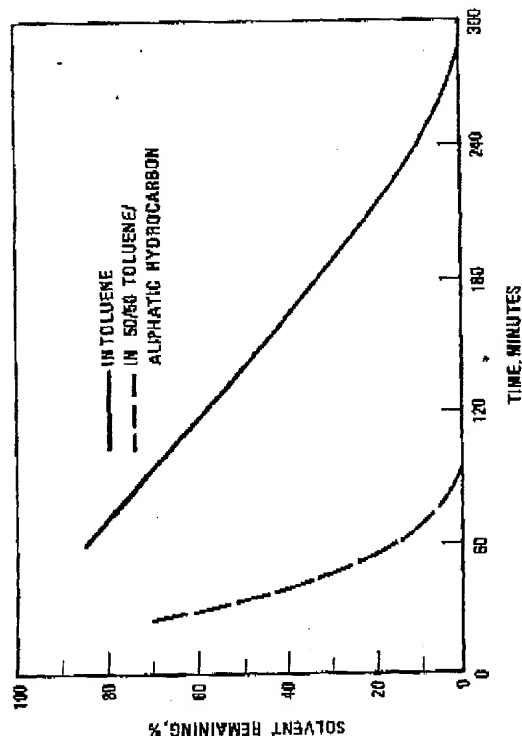


Fig. 11-14. Solvent evaporation rates for 10%W solutions of an S-I-S thermoplastic rubber (Kraton® D 1107 Rubber) in toluene or aliphatic hydrocarbon (Shellsol® BT66) solvent.

Hot Melt Behavior of Thermoplastic Rubbers. Heating the thermoplastic rubber above the glass transition temperature T_g of the polystyrene endblocks (about 92°C) "unlocks" the physically crosslinked thermoplastic rubber network. Although the domains soften at temperatures above 92°C, the act of heating alone will not cause thermoplastic rubber to melt and flow, and the polymer remains very viscous. It will not flow unless mechanical energy is applied. It should be emphasized that phase interflow cannot be achieved without mechanical mixing even by greatly increasing the temperature. Instead, the rubber phase will begin to decompose at temperatures above about 220°C. Application of shear stress then makes mixing possible with other materials, as the melt viscosity decreases as the shear stress or shear rate increases (Figs. 11-15 and 11-16).

With commercial unsaturated midblock S-B-S and S-I-S thermoplastic rubbers, 120 to 180°C is the normal range for mixing and application. Temperatures above 180°C may lead to excessive oxidative degradation of the rubber network and above 220°C to thermal decomposition. At temperatures below 120°C, the viscosity becomes so high that mechanical breakdown of the thermoplastic rubber may occur. Since oxidative degradation is reduced by lowering temperature, the preferred mixing method is in high shear equipment at 135 to 160°C.

High Shear Melt Mixing Precautions. Thermoplastic rubbers, particularly those with the highest melt viscosities, may build up excessive temperatures in high shear internal mixers (e.g., Banbury mixers) if exposed to the high shear conditions in the absence of plasticizers and stabilizers. Certain precautions should be noted. While mass temperatures up to 180°C are normal in the mixing of thermoplastic rubber formulations, higher temperatures may indicate too high a melt viscosity or too vigorous a mixing action. If the temperature were allowed to rise uncontrolled in such a situation, vaporization of plasticizer light ends and polymer decomposition could occur, creating a potential fire hazard. Excessive temperatures can be minimized during the mixing operation by adding a resin or plasticizer or by reducing mixer speed. It is often desirable to investigate the mixing characteristics of a new composition on a small scale before undertaking large-scale runs.

Saturated thermoplastic rubbers, because they have an olefin midblock, are substantially more resistant to degradation. They can be held at high temperatures for long periods of time with negligible oxidative degradation. In the absence of oxygen, they begin rapid thermal degradation at temperatures above about 275°C. A temperature of 280°C is considered the maximum for processing the saturated midblock thermoplastic rubber polymers.

Resin used in hot melt mixing can be premelted and in effect become solvents for the polymer. A resin which associates with the polystyrene endblock will therefore act as a solvent for this phase during hot melt mixing and enhance polymer dissolution. As mixing progresses, less mechanical energy is required to cause flow.

Successful mixing of hot melt pressure-sensitive adhesive based on unsaturated midblock thermoplastic rubbers depends on minimizing oxidative degradation by balancing the following variables in all types of mixing equipment and mixing processes:

1. Ensure adequate and uniform heating and shearing to soften and disperse polymers, resins, oils, and other ingredients to a homogeneous pressure-sensitive adhesive
2. Minimize the time and temperature in accomplishing dispersion
3. Minimize exposure of the hot melt to air (oxygen)

Manifestations of poor control and balance include gel and viscosity increase with S-B-S thermoplastic rubbers which tend to crosslink, and loss of network strength, i.e., lower viscosity, poorer holding power, and lower service temperature in finished adhesives through chain scission with S-I-S thermoplastic rubbers.

Melt Rheology of Thermoplastic Rubbers: Effect of Shear Rate, Shear Stress and Temperature. Viscosities of thermoplastic rubbers in the melt state change rapidly with variations in shear rate, shear stress or temperature. As noted previously, thermoplastic rubbers will not melt and flow at mixing or application temperatures if no shear stress is applied, due to the two-phase nature of the polymers.

The effect of shear rate on viscosity at 177°C is shown in Fig. 11-15 for an S-I-S polymer. This illustration shows the highly non-Newtonian behavior of thermoplastic rubbers by the rapid drop in melt viscosity with increasing shear rate. Note that at the shear rate of laboratory instruments (10 sec^{-1}) viscosity would be extrapolated to over $1,000 \text{ Pa} \cdot \text{s}$, but at shear rates encountered in actual mixing and application (10^2 – 10^3 sec^{-1}), it drops substantially.

Thermoplastic rubbers other than the one used in Fig. 11-15 would produce similar melt viscosity curves. Generally, for a higher molecular weight thermoplastic rubber or for the saturated midblock thermoplastic rubbers, the entire curve would be moved upward; for a lower molecular weight thermoplastic rubber, it would be moved downward.

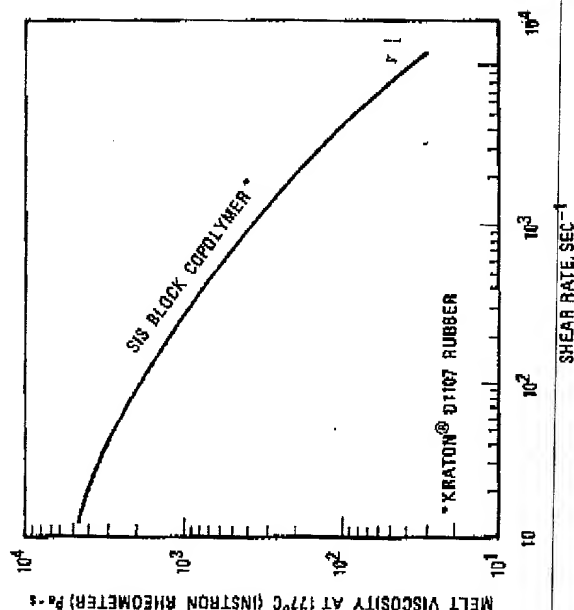


Fig. 11-15. Melt viscosity versus shear rate for a neat S-I-S polymer.

The effect of shear stress on melt viscosity is illustrated in Fig. 11-16 for an S-B-S thermoplastic rubber. Melt viscosity is shown to decrease nearly a hundredfold with increasing shear stress. This figure also shows the changes in melt viscosity effected by temperature. At a constant 0.7 MPa (10^2 psi) shear stress (the force exerted at melt flow condition G in a melt flow apparatus, ASTM Method D1238), a change of about 30°C will have a three-fold effect on viscosity.

At temperatures approaching the glass transition temperature of the polystyrene endblock, melt viscosity changes more rapidly with temperature, particularly at low shear rates. Figure 11-17 shows the effect of temperature on melt viscosity at constant shear rates for an S-B-S thermoplastic rubber.

As shown in Fig. 11-17, the rate of softening in the 80° to 120°C range

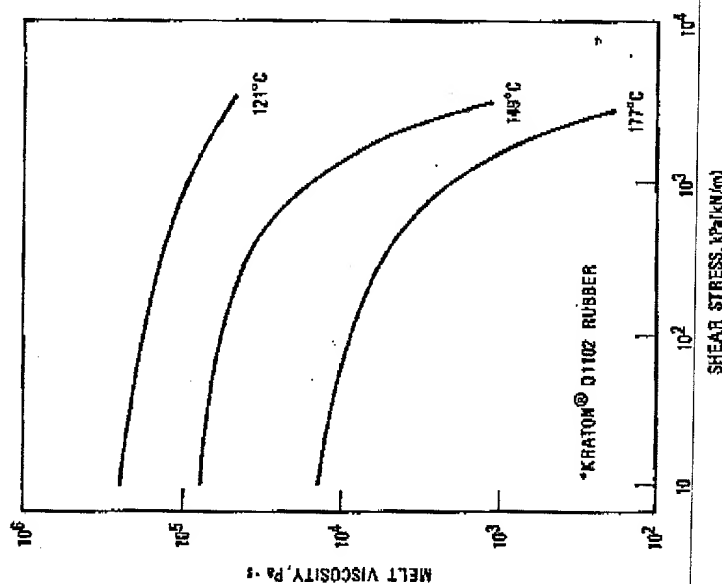


Fig. 11-16 Melt viscosity versus shear stress at constant temperature for a neat S-B-S polymer.

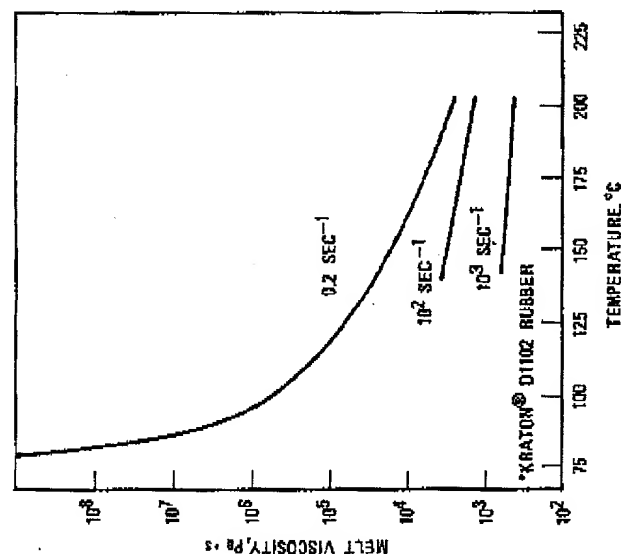


Fig. 11-17. Temperature versus melt viscosity at constant shear rates for a neat S-B-S polymer.

is rapid as the polystyrene endblock domains become fluid. Conversely, on cooling, buildup of viscosity and strength is rapid.

Effect of Resins on Melt Properties. One function of resins is to reduce the viscosity of thermoplastic rubber melts. Even with resins added in, the behavior of thermoplastic rubber compounds is still non-Newtonian, but less so than for the polymer alone as described previously. Illustrative viscosities are shown in Fig. 11-18 for an S-B-S polymer/resin blend.

General Approach to Melt Mixing. Hot melt adhesive blends based on thermoplastic rubbers can be mixed by using a wide variety of batch or continuous mixing equipment. S-B-S and S-I-S polymers dissolve readily in hot resins, with only moderate agitation. Higher molecular weight thermoplastic rubbers require higher shear in mixing. Increasing the surface area of the polymer through granulation substantially reduces the dissolution time in batch mixing equipment. Using both polystyrene-associating resins and rubber-associating resins aids in dissolving both phases of the polymer, permitting faster cycles and reduced mixing temperatures.

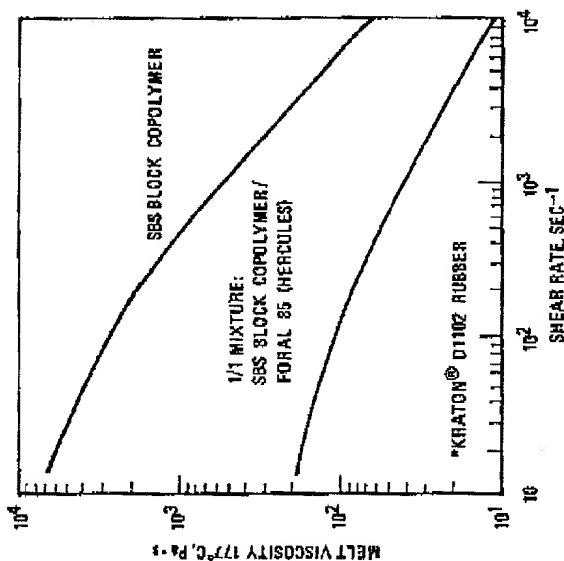


Fig. 11-18. Effect of a rosin-ester resin on the melt viscosity of an S-B-S* polymer at various shear rates.

As in hot melt processing of any type of hydrocarbon material, adhesive degradation can occur, with resultant changes in final properties through chain scission and chain crosslinking reactions of the polymer molecule. This is less of a concern when processing saturated midblock thermoplastic rubbers. The effectiveness of mixers should be judged by their ability to mix the adhesive uniformly and without degradation. Generally, high shear mixers such as twin screw extruders or sigma blade mixers are preferred for mixing because they can give homogeneous mixes in short periods of time, minimizing product degradation. For formulations in which degradation must be minimized, adhesives based on unsaturated thermoplastic rubbers must be protected against oxidative degradation by blanketing with an inert atmosphere.

Degradation and Protection During Processing: The manufacture of thermoplastic rubber-based melt formulations normally takes place in the range of 120 to 180°C. The primary factor in degradation is oxygen attack, which in melt mixing is accelerated by high temperature and high shear conditions. In addition, other hazards exist in melt processing and general handling of thermoplastic rubber crumb as previously discussed.

One approach to minimizing degradation is to reduce temperatures or shear rates where they are extreme. However, the most direct and most effective method of preventing degradation under melt mixing application conditions is to exclude oxygen. Contact with air is obviously greatest in open pot type mixers, less in closed equipment such as continuous feed extruders.

Blanketing or continuous purging of the mixing equipment or hot storage pots with N_2 , CO_2 , or other inert gas will significantly reduce oxidative degradation and should be considered mandatory. Even an initial purge of the mixer or storage vessel may be quite beneficial.

Figure 11-19 demonstrates the protection possible through inert gas blanketing. These data were derived from testing of an S-I-S based adhesive mixed in a Brabender Plasti-Corder (C. W. Brabender Instrument, Inc.) equipped with a high shear sigma blade mixing head. The illustration shows that with air present, viscosity decreases rapidly in proportion to shear applied and residence time in the mixer. Melt viscosity remains nearly constant at both shear rates when N_2 is purged through the mixing head.

Figures 11-20A and 11-20B demonstrate the beneficial effect N_2 blanketing has in preventing degradation of an S-I-S polymer-based pressure-sensitive adhesive when held in a melt holding tank for extended periods of time at elevated temperature. Severe decreases in melt viscosity and adhesive holding power are shown after less than 24 hours when the adhesive is in contact with air (Fig. 11-20A); the same adhesive when N_2 blanketed

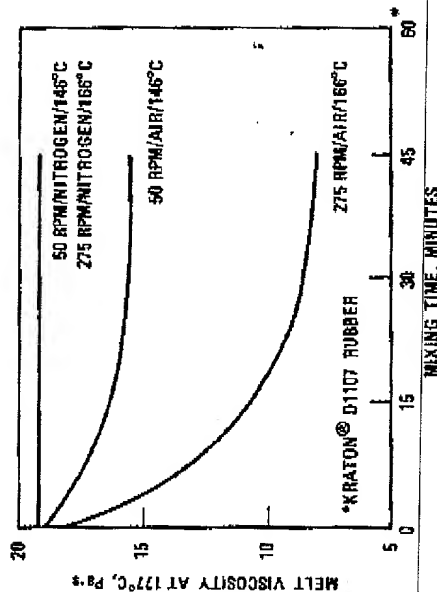


Fig. 11-19. Effect of mixing conditions on melt viscosity retention of a pressure-sensitive adhesive based on an S-I-S polymer.*

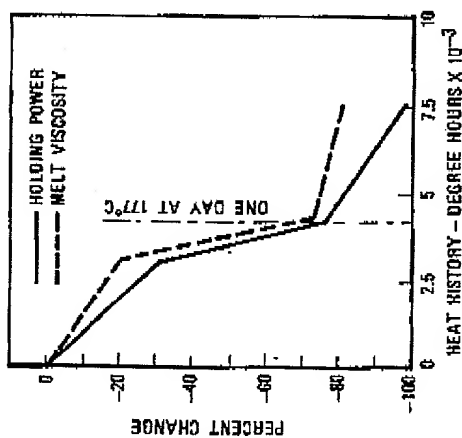


Fig. 11-20A. Hot melt pressure-sensitive adhesive pot life study in contact with air at 177°C.

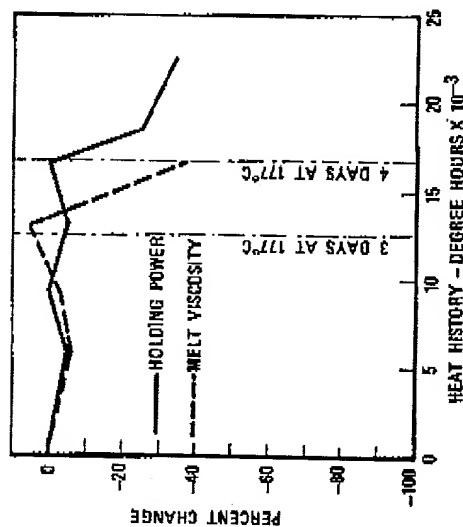


Fig. 11-20B. Hot melt pressure-sensitive adhesive pot life study under nitrogen blanket at 177°C.

shows little reduction in viscosity and holding power for over 72 hours under the same conditions (Fig. 11-20B).

Figure 11-21 shows general trends of adhesive properties for an S-I-S polymer system as degradation proceeds. Tack and adhesion values change

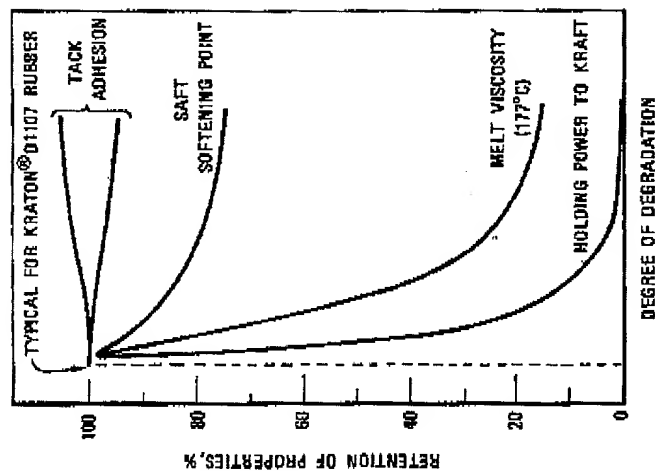


Fig. 11-21. Effect of degradation on retention of pressure-sensitive adhesive properties based on an S-I-S polymer.

little, with tack improving slightly. Thus, measurement of these properties of the finished product are not useful in measuring degradation. Reduction of melt viscosity is often a desirable goal in formulating. However, it is also a manifestation of chain scission of the S-I-S polymer when uncontrolled degradation has occurred in mixing, with resultant loss of service temperature (SAFT) and holding power to kraft paper adhesive properties.

Finally, qualitative degradation as a function of mixer type and heat history is shown in Fig. 11-22. Clearly, continuous mixers and high shear batch mixers are preferred (minimal heat histories to accomplish mixing). Where low shear batch mixers must be used, then residence times in mixing are longer, and the beneficial nature of N_2 blanketing of the system again becomes apparent.

Adhesive Product Manufacture

Solvent applied thermoplastic rubber formulations employ equipment used to coat conventional solution rubbers.

Table 11-8. General-purpose tape formulation and properties based on an S-I-S thermoplastic rubber.

FORMULATION NO. 7	PARTS BY WEIGHT
S-I-S polymer ^a	100.0
Hydrocarbon tackifying resin ^b	140.0
Paraffinic/naphthenic oil ^c	10.0
Zinc dibutyl dithiocarbamate	5.0

ADHESIVE PROPERTIES	TARGET	FORM NO. 7	TARGET	FORM NO. 7
Coat weight (g/m ²)	—	43.0	—	36.0
Rolling ball tack (cm)	1.0	1.3	1.5	1.3
Polyken probe tack (kg)	0.3	0.6	1.0	1.3
180° peel strength (N/m)	400	550	500	800
SAFT to Mylar °C	60	71	93	85
SAFT to kraft °C	54	61	65	67
Holding power (shear) to steel (min) ^d	200	500	2000	2000
to kraft (min) ^d	175	300	2000	2000
Box loop test (days)	10	> 30	> 30	> 30

HOT MELT COATED TAPES

CREPE PAPER

POLYESTER

^a Kraton D-1107 rubber; Shell Chemical.^b Such as: Escorez 1310, Exxon Chemical or Winglack 95, Goodyear Chemical, or other 100°C softening point C₃ resins.^c Shellflex 371; Shell Chemical.^d 12.7 × 12.7 mm contact, 1 kg load.

formulation provides a good balance of properties for general-purpose crepe or polyester tapes.

Using the concepts of contour diagramming and investigating specific formulations, it is possible to adjust the resulting adhesive properties to meet a wide variety of performance properties. However, in all cases, care must be taken to prevent degradation of the adhesive to ensure uniform and reproducible adhesive properties. Hot melt viscosity, shear strength, and bleed and high-temperature performance are adversely affected by adhesive degradation. But with proper precautions, such as inert gas blanketing and minimal heat history of the adhesive, reproducible, high-quality tapes and labels can be produced as a 100% solids hot melt system.

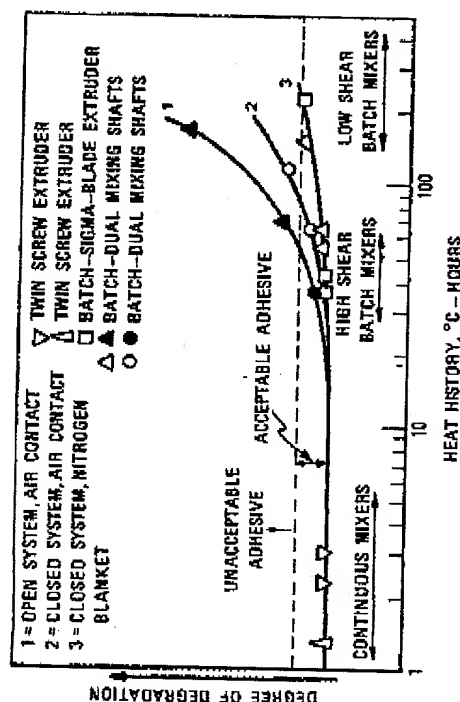


Fig. 11-22. Effect of heat history on degree of degradation for a pressure-sensitive adhesive based on an S-I-S polymer using various hot melt mixing equipment.

Dip roll, slot-die and extrusion types of equipment can be used to apply hot melt pressure-sensitive adhesives based on thermoplastic rubbers. Dip roll and slot-die coaters involve the use of a reservoir of molten adhesive as a supply for the coating head; the extrusion process is a continuous one, with adhesive mixed and fed to the coating head directly.

FORMULATING TO MEET CONSTRAINTS

This section is devoted to discussion of examples of formulating technology and performance of thermoplastic rubber in a wide span of end-use target requirements. It serves the primary purpose of showing what can be done with thermoplastic rubbers as formulated pressure sensitive-adhesive compositions. It serves the secondary purpose of guiding initial thought in considering the kinds of tape and label applications and products in which thermoplastic rubbers can be useful as pressure-sensitive adhesives.

General-Purpose Tapes

Having established the performance and end-use requirement targets for crepe paper and polyester tapes, the formulation shown in Table 11-8 is typical. This formulation has demonstrated a balance of pressure-sensitive properties when properly coated on a commercial type coater to commercially available backings. As the reference data in Table 11-8 show, this

Most duct tape is made using a calendaring process, with natural rubber as the major base polymer in the pressure-sensitive adhesive. The adhesive mass is applied solventless, and is not further heat treated. This solventless method is used because the adhesive coat weight is high, and efficient solvent removal via forced drying at temperatures below the melting point of polyethylene is difficult and expensive. High coat weights are necessary in order to ensure good adhesive coverage of the open weave cloth scrim, and to form a functional, continuous layer of pressure-sensitive adhesive for bonding.

Properties of duct tape made via the hot melt process with block copolymer as the sole adhesive base polymer are shown in Table 11-10, and are compared in standard tests with four commercial calendared duct tape constructions.

High-Temperature Tapes via Crosslinking

Pressure-sensitive adhesives based on thermoplastic rubbers perform well over the temperature range required in the majority of pressure-sensitive product applications. However, as the temperature at which the product will be used approaches the glass transition temperature of the endblock phase of the rubber (about 92°C), the polystyrene endblock domains begin to soften and unlock the physical crosslinks. When this occurs, the rubber midblocks are no longer crosslinked and the adhesive shows a drastic reduction in cohesive strength. Therefore, adhesives based on thermoplastic rubber cannot be used, for example, on high-temperature masking tapes which must withstand a significant load at temperatures in paint baking ovens of up to 170°C. This limitation can be overcome by chemically crosslinking the rubber in the adhesive so that it will no longer be thermoplastic.

The double bonds in the midblocks of the unsaturated S-B-S and S-I-S polymers provide sites for chemical crosslinks. These unsaturated thermoplastic rubbers can be crosslinked with the usual sulfur, sulfur donor, or peroxide curing systems traditionally used for crosslinking unsaturated rubbers. There are many combinations of ingredients which could be used in a sulfur-based crosslinking package. For example, the crosslinking package could contain 0.3-1.5 phr of elemental sulfur or a sulfur donor (e.g., Sulfads), 0.3-1 phr of an accelerator (e.g., Altax or Methyl Zimate) and 0.3-1 phr of ZnO and stearic acid. A peroxide crosslinking system could contain 1-4 phr of peroxide (e.g., Di Cup) and could be used in combination with 5-25 phr of a reactive acrylic monomer (e.g., Sartomer SR 351). Either the sulfur or the peroxide crosslinking package can be mixed directly into the adhesive solution. Crosslinking occurs thermally as the adhesive tape passes through the solvent evaporation ovens.

General-Purpose Permanent Labels

Adhesives for labels have different requirements than tapes and should be formulated accordingly. Labels have lower cohesive strength than tapes, but the adhesive should not bleed through the label stock when exposed to temperatures of 60°C for 2 to 3 weeks. Higher levels of resin and/or plasticizer can be used in label formulations to help lower the cohesive strength and reduce formulation costs.

New polymers, such as Kraton DX-1112 rubber, have been developed specifically for adhesives where low cohesive strength and lower viscosity is desired. The formulation shown in Table 11-9 demonstrates a balance of pressure-sensitive adhesive properties and die cuttability when using Kraton DX-1112 rubber in this formulation.

General-Purpose Duct Tape

Duct tape is the familiar silver colored polyethylene/cloth laminated pressure-sensitive product. Its name is derived from the major intended use it serves—to wrap air conveying ducts, keeping insulation positioned in place. It is also a popular tape product with the general public for a variety of patching jobs around the home and at work.

Table 11-9. Comparison of two linear S-I-S thermoplastic rubber polymers for permanent labels.

BASE POLYMER ADHESIVE PROPERTIES	KRATON D-1107		KRATON DX-1112	
	RUBBER FORMULATION*	RUBBER FORMULATION*		
Rolling ball tack (cm)	20	10		
Loop tack (N/m)	500	550		
Polyken probe tack (g)	400	500		
Holding power (shear) to steel (min)*	200	170		
Bleed (3 weeks at 60°C)	None	None		
Die cuttability	Fair-Good	Good		
Formulation	Parts by weight			
Kraton rubber	100.0			
Hydrocarbon tackifying resin	150.0			
Shellex 371 oil	50.0			
Zinc dibutyl dithiocarbamate	5.0			

* 12.7 × 12.7 mm contact, 500 g load.

Table 11-11. Pressure-sensitive adhesive cross-linked with phenolic resin.

S-I-S polymer ^a	100
C ₃ Resin ^b	50
Phenol-formaldehyde resin ^c	20
Zinc resinate ^d	10
Zinc dibutyl dithiocarbamate	2
2,5-di(tert-amy) hydroquinone ^e	1
% solids in toluene	50

^a Kathon D-1107 rubber, Shell Chemical.
^b Wingrask 95, Goodyear.
^c Amberol ST-137, Rohm and Haas.
^d Reichhold Chemical, Newport Division.
^e Santovar A, Monsanto.

Another approach to improve the high-temperature cohesive strength of adhesives based on thermoplastic rubber is by establishment of a thermoset network extending throughout the rubber phase. This can be accomplished by the use of reactive phenolic resins in combination with a metal catalyst. An example of a formulation which is claimed to be effective is given in Table 11-11. This type of crosslinking system can be mixed directly into the adhesive solution. Crosslinking is initiated thermally in the solvent evaporation ovens.

A thermally-initiated crosslinking reaction would almost always be used to crosslink an adhesive applied from solvent because crosslinking can be conveniently initiated in the solvent evaporation ovens. However, thermally-initiated crosslinking systems present considerable handling problems for hot melt adhesives in that they may crosslink the adhesive in the hot melt processing equipment. A crosslinking system which can be initiated by exposure to radiation is a more practical route to crosslink a hot melt adhesive. The formulations shown in Table 11-12 are two which can be crosslinked by exposure to radiation. The reactive monomer, SR-350 (trimethylolpropane trimethacrylate), is needed in the formulation to reduce the radiation dose required to achieve crosslinking of the adhesive. Both adhesive formulations in Table 11-12 tend to crosslink when held at hot melt processing temperatures. However, both adhesives crosslink slowly enough that they can be extrusion coated onto the tape substrate before significant crosslinking has occurred. Formulation A in Table 11-12 can be crosslinked by exposure under a N₂ blanket to electron beam radiation at a dose of 2 to 6 megarads. Formulation B in Table 11-12 contains a photoinitiator, Irgacure 651, in addition to the reactive monomer. The function of the photoinitiator is to dissociate rapidly under exposure to UV light to generate free radicals which initiate the crosslinking reaction. Formulation

Table 11-10. Thermoplastic rubber pressure-sensitive adhesive duct tape vs. commercial duct tape products.

IDENTIFICATION PROPERTIES	HOT MELT THERMOPLASTIC RUBBER ^a		COMMERCIAL DUCT TAPES	
	LOW COAT	HIGH COAT	A	B C D
Substrate	Joanna Western ^b	Joanna Western ^b	PE film/cloth scrim	PE film/cloth scrim
Release coat	None	None	—	—
Adhesive coat weight (g/m ²)	124	210	—	204
Rolling ball tack (cm)	1.2	0.5	0.9	0.8
Polyken probe tack (kg)	0.6	0.9	0.5	0.8
SAFT to Mylar (°C)	74	81	75	42
SAFT to kraft (°C)	77	77	61	40
180° peel to steel (N/m)	1460	2100	370	390
180° peel to backing (N/m)	790	1320	230	300
Quick stick to steel (N/m)	820	1020	230	300
Holding power to kraft (min)	165	160	10	1
12.5 × 12.5 mm, 2 kg load	4450	5470	90	31
12.5 × 12.5 mm, 1 kg load	120	55	40	5
Box loop test, days to failure	> 35	> 35	80	< 1
25 mm test strip	> 35	> 35	< 1	< 1
12.5 mm test strip	> 35	> 35	< 1	< 1

^a Formulation: 100 parts Kathon D-1107 rubber, 140 parts Wingrask Plus, 10 parts Shellflex oil, 5 parts Butzara, 5 parts TiO₂.
^b Prelaminated polyethylene/cloth scrim made by Joanna Western Mills Co., Industrial Products Division.

Tabl 11-12. Pressure-sensitive adhesive formulations cross-linked by exposure to radiation.

	A	B
S-I-S polymer ^a	100	100
C ₃ tackifying resin ^b	100	80
Paraffinic/naphthenic oil ^c	25	—
Multifunctional coupling agent ^d	25	25
UV initiator ^e	—	6
Zinc dibutyl dithiocarbamate	2	1

^a Kraton D-1107 rubber, Shell Chemical.

^b Winglack 95, Goodyear.

^c Shellflex 371 oil, Shell Chemical.

^d SR-350, Sarcosine (trimethylolpropane trimethacrylate).

^e Irgacure 651, Ciba-Geigy (acrylophenone).

B in Table 11-12 can be crosslinked by exposure under a N₂ blanket to UV light at the dose achieved by passing the adhesive under two 200-watt/in. medium-pressure Hg lamps at a line speed of 20 m/min. However, it is required that the light be filtered to remove the portion of the spectrum whose wavelength is less than 320 nm in order to prevent degradation of the surface of the adhesive.

Because their midblock is saturated, the S-EB-S and S-EP-S polymers are much more difficult to crosslink. A formulation similar to formulation A in Table 11-12 containing an S-EB-S polymer rather than an S-I-S polymer cannot be crosslinked at commercially acceptable rates by exposure to UV light. It can be crosslinked by exposure to electron beam radiation but doses of at least 6 megarads are required.

It must be noted that while crosslinking an adhesive based on a thermoplastic rubber brings about the desired improvement in high-temperature cohesive strength, it also causes a reduction in aggressive tack of the adhesive. Unless the rubber has been designed specifically for use in crosslinked adhesives, chemical crosslinking of a thermoplastic rubber corresponds roughly to overcuring a conventional rubber vulcanizate. This reduction in aggressive tack can be partially offset by including a plasticizer in the adhesive formulation.

Low-Temperature Tapes and Labels

A special type of formulation is required for pressure-sensitives which are used in cold environments, e.g., tapes and labels that are used for frozen food packaging and in some electrical insulating tapes.

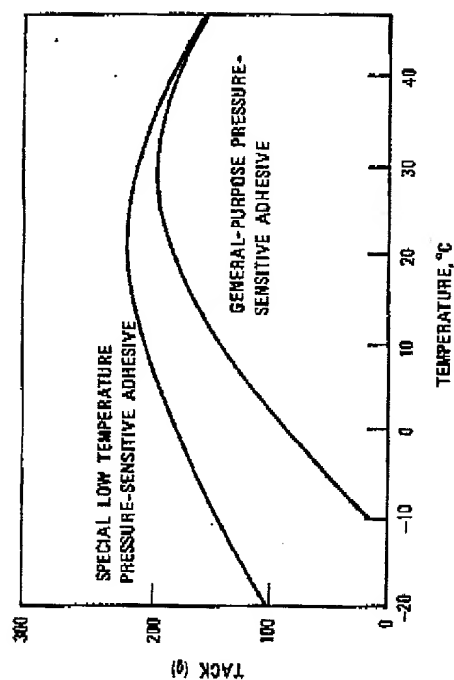


Fig. 11-23. Probe tack as a function of temperature.

Most adhesives lose their tack and adhesion properties as temperature decreases as depicted in Fig. 11-23, which presents the results of probe tack measurement as a function of temperature. If the temperature falls below 20°C, the tack decreases rather sharply. At 0°C, common adhesives are very low in aggressive tack, and at -10°C, they have no measurable tack at all.

This behavior of the adhesive upon lowering the temperature can be readily explained by considering its rheological properties. Tack of an adhesive is related to its modulus. The lower the modulus, the easier the adhesive will be deformed and flow, making good contact with the adherent. The rubber component in a pressure-sensitive adhesive alone has practically no tack. However, decreasing the modulus by addition of sufficient amounts of rubber-compatible resins and plasticizers raises the aggressive tack at room temperature.

The modulus value of the adhesive and thus the tack at any given temperature is highly dependent on the glass transition temperature of the rubber component T_g and the glass transition temperature of the adhesive composition T_g' . These effects are shown schematically in Fig. 11-24. As the temperature decreases the modulus increases. The adhesive becomes less able to flow and make contact with the substrate. At or below T_g' , the adhesive behaves as a rigid solid and the tack will be nil. It is clear that the lower the T_g' of an adhesive, the longer the tack properties will be maintained with a decrease in temperature.

The T_g of elastomers is rather low. For polyisoprene and polybutadiene, midblock components in unsaturated thermoplastic rubbers, T_g 's

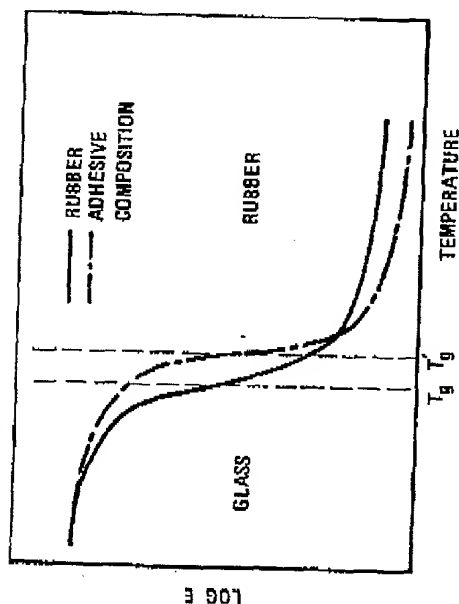


Fig. 11-24. Schematic presentation of modulus, E , as a function of temperature and pressure-sensitive adhesive glass transition temperature (T_g).

are -58 and -91°C , respectively. However, when midblock associating resins are added, to obtain tack at ambient temperature, the T_g of the composition increases rapidly with increasing resin content (T_g to T_g^* shift illustrated in Fig. 11-24). The extent of this shift depends on the type of resin and plasticizers incorporated, and the resultant T_g value of the ultimate adhesive blend.

By using materials with a relatively low T_g and low rate of change in modulus with temperature, adhesives can be formulated with good low temperature tack. However, to maintain the ambient temperature properties, careful selection of all ingredients is necessary.

To predict the presence of tack at low temperature for a given adhesive formulation, it will be useful to know its T_g^* . Equation (3) can be used to predict the T_g of a blend of fully compatible ingredients from the T_g values of the separate components.⁴ Hence,

$$\frac{1}{T_g} = \sum_{i=1}^n \frac{W_i}{T_{gi}} \quad (3)$$

where T_g = glass transition temperature ($^\circ\text{K}$) for the adhesive blend

T_{gi} = glass transition temperature ($^\circ\text{K}$) for component i

W_i = weight fraction of component i

If the T_g of the components are known, the T_g of the adhesive formulation can be calculated and the lowest temperature at which tack could be expected is then known. In Table 11-13, the calculated T_g for a number of adhesive formulations based on an S-I-S thermoplastic rubber are presented together with their low-temperature tack values.

S-I-S block copolymers show two T_g 's, i.e., one corresponding to their polystyrene phase (92°C) and one to their rubber phase (-58°C for polyisoprene). Because the low-temperature performance is determined by the latter, this value is used in the calculation.

A probe tack test was used to measure the tack at the low temperatures. In this test, a flat-ended stainless steel probe was contacted under a light weight with the adhesive surface for a very short time. The force required to withdraw the probe was measured. From the table, it can be seen that measurable tack is developed as long as the test temperature is above the T_g of the given adhesive formulation.

Contour diagrams presenting T_g for adhesive formulations as a function of type and amount of the ingredients can be very helpful to predict formulations with good low-temperature properties. In Fig. 11-25, an example is given for a combination of linear S-I-S polymer, Wingtack 76 as

Table 11-13. Low temperature tack and T_g for a number of S-I-S based pressure-sensitive adhesives.

COMPONENTS	T_g ($^\circ\text{C}$)	COMPOSITION					
PROPERTIES	UNITS						
S-I-S Polymer ^a	-58	100	100	100	100	100	100
Wingtack 95	51	80	—	—	125	—	125
Wingtack 76	32	—	80	—	—	125	—
Wingtack 10	-28	—	—	80	—	—	—
Stellflex 371 ^d	-64	—	—	—	25	25	—
Indopol 150 ^e	-80	—	—	—	—	—	50
T_g (calculated)	$^\circ\text{C}$	-16	-22	-45	-12	-19	-23
Probe Tack at:							
-12°C	(g)	150	180	—	35	160	225
-18°C	(g)	6	190	290	0	60	180
-29°C	(g)	—	—	310	—	—	—

^a T_g value measured by DSC.

^b Kathon D-100 rubber; Shell Chemical (isoprene midblock T_g).

^c Hydrocarbon resin, Goodyear.

^d Paraffinic/aromatic processing oil, Shell Chemical.

^e Low molecular weight polybutene, Amoco.

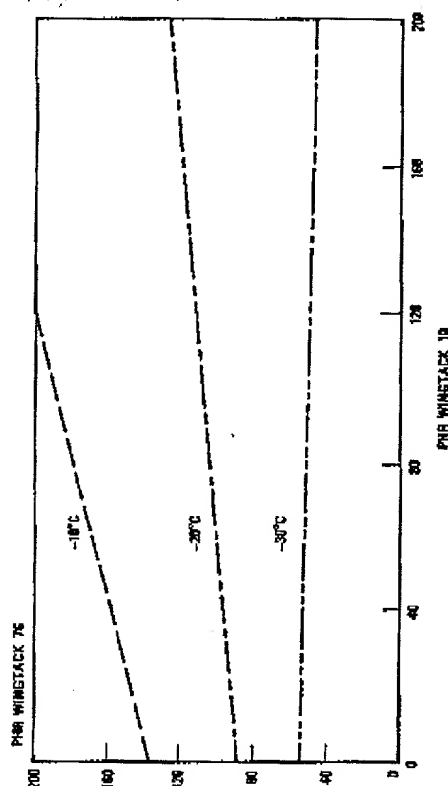


Fig. 11-25. Contour isopleths for calculated glass transition temperature (T_g) for two resins in an S-I-S polymer (Kraton® D 1107 Rubber) based system.

tackifying resin and Wingtack 10 as plasticizer. From this figure, it is easy to find formulations in which tack could be expected down to -30°C .

However, other property requirements, such as melt viscosity, ambient tack properties, peel adhesion, and holding power limit the area from which an adhesive for low-temperature tack can be chosen. Formulations with a relatively low amount of high softening resin and a relatively high amount of plasticizer may fulfill both the requirement for low-temperature tack and low melt viscosity. However, 180°C peel adhesion and holding power will be unacceptably low.

By superpositioning of the contour diagram for T_g with those for the other critical properties, it may be possible to choose a proper formulation with a satisfactory balance in properties, including low-temperature performance.

In Table 11-14, a number of adhesives, which were selected in that way, for low-temperature labels is presented together with the values of the most critical properties.

Weatherable Tapes

Pressure-sensitive adhesives are acceptable for a wide variety of applications. However, only those polymers that are fully saturated can offer excellent resistance to degradation by air, ozone or UV light. Kraton G thermoplastic rubbers have a saturated rubber midblock and, when formu-

lated with saturated resins, plasticizers and stabilizers, can obtain a balance of adhesive properties as well as resistance to degradation by oxidation or UV light.

The formulation shown in Table 11-15 demonstrates a good balance of adhesive properties in a formulation containing only saturated compounding ingredients. Although the tack of this formulation, as measured by standard tack tests, appears to be very good, its tack in a "thumb appeal" test (a qualitative estimate of tack when touched under mild pressure with one's finger) is only fair.

The UV resistance of two adhesives based on saturated formulating ingredients was compared in an accelerated weatherometer test with the resistance of an adhesive based on unsaturated formulating ingredients. The 180° peel strength of the adhesive cast on polyester backing and adhered to glass was measured as a function of exposure time in a Xe lamp weatherometer. As shown in Table 11-16, the performance of the adhesive based on unsaturated ingredients, formulation A, is poor. In less than six days exposure, the adhesive was so badly degraded that it failed cohesively when

Table 11-14. Selected low temperature pressure-sensitive label formulations.

INGREDIENTS	UNITS	A	B	C	D
S-I-S polymer ^a	(parts)	100	100	100	100
Wingtack 76	(phr)	75	—	—	—
Super Static 80 ^b	(phr)	—	62.5	—	—
Escorez 1310 ^c	(phr)	—	—	50	—
Wingtack 95	(phr)	—	—	—	50
Wingtack 10	(phr)	50	62.5	75	100
Zinc dibutyl dithiocarbamate	(phr)	5	5	5	5
PROPERTIES	UNITS	REQUIREMENTS ^d			
T_g (calculated)	($^\circ\text{C}$)	-21	-24	-26	-25
Probe tack at -18°C	(g)	390	420	450	470
Rolling ball tack	(cm)	1.2	1.0	1.1	1.0
Loop tack ^e	(N/m)	540	620	580	700
180° peel adhesion	(N/m)	580	620	660	770
Holding power ^f	(min)	> 1000	> 1000	> 1000	> 390
Melt viscosity at 175°C	(Pa-s)	43	41	43	23

^a Kraton D-1107 Rubber, Shell Chemical.

^b Hydrocarbon resin, Goodyear Chemical.

^c Hydrocarbon resin, Reichhold Chemical.

^d Hydrocarbon resin, Exxon Chemical.

^e As measured on available commercial labels.

^f To steel, 25×25 mm contact area.

^g Polyester film to steel, 1 kg load, 12.5×12.5 mm contact area.

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peeled from the glass. As exposure is continued, the peel sample continues to fail cohesively, but at lower and lower peel strengths as the cohesive strength of the adhesive is further reduced by degradation.

The UV resistance of the adhesives based on saturated ingredients, formulations B and C, is much better than that of formulation A in Table 11-16. In fact, these adhesives appear to weather better than the polyester backing since, after extended exposure, the backing tears during the peel strength measurement.

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Table 11-15. Weather resistant pressure-sensitive adhesive tape based on a saturated S-EB-S thermoplastic rubber.

FORMULATION	DRY WEIGHT (g/ft)
S-EB-S polymer ^a	100
Arkton P85 ^b	115
Tuffalo 6056 ^c	15
Irganox 1010 ^d	1
Tinuvin 327 ^e	0.25

ADHESIVE PROPERTIES	
Coat weight (g/in ²)	35
Rolling ball tack (cm)	2
Polyken probe tack (kg)	0.9
180° peel strength (N/m)	550
SAFT to Mylar (°C)	80
Holding power to kraft (min)	150
Melt viscosity @177°C (Pa-s)	60

^a Kraton GX-1657 rubber, Shell Chemical.
^b Saturated aliphatic hydrocarbon resin, Arakawa.
^c Atlantic Richfield Co.
^d Ciba-Geigy Co.

Table 11-16. UV resistance: saturated polymer (S-EB-S) vs. unsaturated polymer (S-I-S) based pressure-sensitive adhesive tapes.

EXPOSURE TIME ^a (days)	180° PEEL STRENGTH (N/m)		
	FORMULATION A ^b	FORMULATION B ^b	FORMULATION C ^b
0	840	510	550
6	1000-2000 Coh ^c	610	700
13	880-1600 Coh	650	800
21	860 Coh	770	Tear ^d
31	930 Coh	1030	Tear
42	530 Coh	Tear ^d	Tear
63	0 Coh	1120	Tear

^a 180° peel sample on glass, exposed through glass in Xe lamp weatherometer.

^b Formulations

Formulations	A	B	C
Kraton D-1107 rubber	100	—	—
Kraton GX-1657 rubber	—	100	100
Ecocore 3380	80	80	—
Arkton P85	—	—	115

Tuffalo 6056	—	1	15
Irganox 1010	—	1	1
Tinuvin 327	0.25	0.25	0.25

^c Coh indicates cohesive failure within adhesive layer.

^d Tear indicates polyester (Mylar) backing becomes brittle and tears.